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TOSHIO MASUDA

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CATIONIC POLYMERIZATION OF VINYL ETHERS AND STYRENE DERIVATIVES

— STRUCTURE AND REACTIVITY OF MONOMER AND PROPAGATING SPECIES

TOSHIO MASUDA

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INTRODUCTION

The cationic polymerization of vinyl compound belongs to the reactions in which a linear polymer with carbon skeleton is formed, like radical and anionic polymerizations. In the mechanistic aspect of organic chemistry, the propagation reaction of the cationic polymerization is one of the electrophilic addition reactions to carbon-carbon double bond, and is of the same kind as the addition reaction of a protonic acid or a halogen to an olefin.¹ The propagating species is a carbocation. Therefore, it is in close connection with the intermediate in a solvolysis reaction which is one of the most familiar reactions for a chemist, and with the carbocations which have been extensively studied by Olah and his collaborators.² Further, a variety of Lewis acids and Brönsted acids have been used as the initiator in cationic polymerization, so that the polymerization has some aspects in common to acid-catalyzed reactions like the Friedel-Crafts reaction.³ Thus, cationic polymerization is related to many fields in organic chemistry.

In general, the factors affecting a reaction is divided into two main classes, medium effect and substituent effect.⁴ The former is the effect of external factors such as solvent, catalyst and temperature, and the latter the effect of internal factors, that is, structure of a substrate. In order to study cationic polymerization from the viewpoint of physical organic chemistry and to gain an insight into the reaction mechanism, it is necessary to investigate in detail the influence of these individual factors on the reaction. Especially, studies on substituent effect frequently give a more direct information than those on medium effect do, and play a great role in the

understanding of reaction mechanism. The Hammett rule is representative of the studies, and in consequence has been one of the expressions most frequently used by physical organic chemist. The knowledges on the molecular orbital and molecular properties (ionization potential, excitation energy, bond length etc.) of a compound are indispensable for the sake of deeper and more exact understanding of the substituent effect. Molecular orbital theory has made a rapid progress with the aid of digital computers. For instance, Pople has devised semiempirical LCAO MO methods such as CNDO and INDO, and has succeeded in applying them to many organic molecules.⁵ As to molecular properties, uv and visible spectra give information on the state of conjugation, photoelectron spectroscopy on the ionization potential, and ¹³C nmr on electron distribution. The advance of these instruments seems to promise more direct analyses of molecular structure and properties.

The addition polymerization of a vinyl compound comprises several elementary reactions such as initiation, propagation, termination and transfer reactions. The propagation reaction is the most characteristic of these in polymerization because the polymer is formed thereby. Accordingly, many of the studies on the reaction mechanism have been focused on the propagation reaction. In fact, there have been many investigations on the propagation rate constant in radical and anionic polymerizations. However, very few methods to determine precisely the propagation rate constant have been established in cationic polymerization. This delayed the development in kinetic study of cationic polymerization. On the other hand, the monomer reactivity ratio can be easily determined also in cationic polymerization. This ratio indicates the relative reactivity of two monomers in a propagation

reaction under a given condition. Accordingly, the reactivity in propagation reaction has been successfully discussed in terms of monomer reactivity ratio.

There are a number of compounds which possess a carbon-carbon double bond polymerizable by cationic mechanism. These include alkyl vinyl ethers, styrene derivatives, N-vinyl-carbazole, indene, cyclopentadiene, and isobutene. Of these monomers, an alkyl vinyl ether is a typical monomer which has a polar substituent, and styrene is a representative monomer which has a conjugating substituent. Therefore, their behaviors in cationic polymerization could be different from each other. It would be of great interest to compare the nature of these monomers and their behaviors in cationic polymerization.

Not only a monomer but also a propagating carbocation and a counterion participate in the propagation reaction of cationic polymerization. Taking account of this, an investigation on the properties of a propagating species will be no less important than a study on the structure and the reactivity of a monomer in order to elucidate the reaction mechanism. However, a direct study of the nature of active species is most difficult. In this respect, a study on salt effect in cationic polymerization seems to be attractive, because the effect of added salt has been evidenced in a number of ion-molecule reactions.

On the basis of the viewpoint mentioned above, the present investigation deals with three subjects on the cationic polymerization of vinyl monomers: 1) studies on the difference in behaviors of alkyl vinyl ethers and styrene derivatives in cationic polymerization by means of copolymerization, 2) studies on the change in reactivity of alkyl vinyl ethers and styrene derivatives caused by substituent, and 3) studies on the

dissociation of a propagating ion pair by means of the salt effect on the reaction rate and on the molecular weight distribution of the polymer obtained.

In the studies described in Part I, the mechanism of propagation reaction of an alkyl vinyl ether and styrene derivatives is investigated by means of copolymerization. As the first investigation on the copolymerization of monomers having different substituents, Overberger, et al., have carried out the cationic copolymerization of isobutene and p-chlorostyrene.⁶ They clearly showed the difference in behaviors between these two compounds. In the succeeding chapters, 2-chloroethyl vinyl ether is employed as a vinyl ether, and p-methoxystyrene, α -methylstyrene and p-methylstyrene as styrene derivatives. This choice of monomers was made to use a vinyl ether and styrene derivatives possessing close reactivities each other, since vinyl ethers are usually more reactive than styrene derivatives.

In Chapter 1, the formation of true copolymers in the copolymerization was confirmed at first. For, attempts of ionic copolymerization of monomers possessing very different structures sometimes result in a mixture of two homopolymers. Next, the shape of copolymer composition curves was investigated, and the large dependence of the relative reactivity on the reaction condition was shown.

In Chapter 2, the temperature dependence of monomer reactivity ratios in these systems was examined. When styrene or a vinyl ether was copolymerized with a homologue, there was almost no temperature dependence. On the contrary, remarkable temperature dependences were observed when a vinyl ether was paired with a styrene derivative. The differences in the activation enthalpy and the activation entropy between both types of compounds were evaluated from the temperature dependence of the monomer reactivity ratios.

In Chapter 3, the effects of catalyst and solvent on the relative reactivity in the copolymerization were investigated. When a strong catalyst and/or a polar solvent are used, a propagating ion pair is thought to be more dissociable. Under these conditions, styrene derivatives proved to have large reactivities. To interpret the experimental result the propagation reaction was tentatively divided into two steps, and the behavior of both monomers in each step was discussed.

Part II is concerned with the substituent effects on the cationic polymerization of alkyl vinyl ethers and styrene derivatives. Introduction of a substituent usually brings about an appreciable change in the reactivity of a compound, and a part of the change must be a reflexion of the nature of transition state of the reaction. However, it should be taken into account that electronic and steric effects of the substituent are always involved. In the following chapters, the change in reactivity with introduction of a substituent is studied in considerable detail.

In Chapter 4, the reactivities of the β -alkyl-substituted vinyl ethers and styrene derivatives were compared with unsubstituted ones. The dependence of the relative reactivity on the nature of solvent and catalyst, and on temperature was large and evident. In every case, the reactivity of β -substituted monomers became close to that of unsubstituted ones under conditions which promote the reaction. The results were explained in terms of the reduction of selectivity and the localization of charge.

In Chapter 5, the reactivities of α -methyl-, α -ethyl-, α -ethoxy- and α -phenyl-substituted vinyl ethers and styrene derivatives were studied. The substituents influenced the reactivity not only electronically but also sterically. Due to

the steric hindrance of α -substituents in propagation reaction, it was difficult to obtain high polymers in homopolymerization of these monomers except α -methyl-substituted ones. In some cases alternating copolymers were produced in the copolymerization with corresponding unsubstituted monomers. The changes in reactivity with the introduction of an α -methyl group in several electrophilic reactions were summarized and discussed.

In Chapter 6, the structure and reactivity of five kinds of 2-alkoxybutadienes were studied. 2-Alkoxybutadiene did not form a high polymer in homopolymerization. The alkoxybutadienes were copolymerized with ethyl vinyl ether. 2-(tert-Butoxy-)butadiene showed peculiarities in copolymerization behavior and molecular properties, which were ascribed to the bulkiness of the substituent.

In Chapter 7, the polar bromination reaction of vinyl ethers and styrene derivatives was studied and compared with cationic polymerization. A considerable increase in reactivity was observed on α -methyl substitution, while the change in reactivity with β -methyl substitution was small. From the results obtained, it was concluded that the polar bromination reaction is very similar to the propagation reaction in cationic polymerization among many electrophilic addition reactions to carbon-carbon double bond.

Part III describes the relationship between molecular orbital or molecular properties and the reactivity of olefins in cationic polymerization. To elucidate a reaction mechanism, it will be very useful to investigate the substituent effect on molecular orbital and molecular properties.

In Chapter 8, a few models of the transition state of propagation reaction in cationic polymerization were proposed and examined on the basis of the calculation by the extended Hückel method. The reactivities of vinyl ethers, propenyl ethers and 1,2-dialkoxy-

ethylenes were invoked to test the models proposed.

In Chapter 9, the relationship between molecular orbital, ionization potential or ^{13}C nmr chemical shift of various monomers and the reactivity in cationic polymerization was studied. When a methyl group is introduced into α - or β -position of ethyl vinyl ether and styrene, remarkable changes in their reactivity and molecular properties were observed. The reaction mechanism in cationic polymerization was discussed on the basis of the intimate correlation observed between the reactivity and molecular properties.

Part IV deals with the studies on the nature of a propagating species. For this purpose, the salt effect on the reaction rate and on the molecular weight of polymers produced was investigated. It is well known that an added salt has a large influence on an ionic reaction, and studies on the salt effect are frequently made to clarify the nature of active species. Studies on salt effect seem to be meaningful also in cationic polymerization. But it must be kept in mind that deliberate analysis of the experimental results is required in cationic polymerization because it comprises a variety of elementary reactions.

In Chapter 10, salt effects on reaction rate and on molecular weight in cationic polymerization were studied for several of the most usual catalysts. Furthermore, salt effect on copolymer composition in the copolymerization of a vinyl ether and a styrene derivative was examined. Conspicuous influences of the added salt were explained principally in terms of exchange of a counterion.

In Chapter 11, the inference drawn in Chapter 10 was ascertained by using iodine, a relatively weak catalyst. The presence

of a salt of an acid stronger than the catalyst used will lead to an increase of reaction rate and molecular weight. As was expected, the rate of the iodine-catalyzed reaction increased remarkably with the addition of tetra-n-butylammonium perchlorate or fluoroborate. This result supports the exchange of a counterion or the metathesis between catalyst and salt.

In Chapter 12, the molecular weight distribution of polystyrene obtained by various catalyst systems was studied. Firstly, by use of either two catalysts or a catalyst and a salt, a polymerization system in which two counterions coexist was devised, and the molecular weight distribution of the polymers formed was examined. Secondly, it was found that molecular weight distribution of polystyrene obtained by acetyl perchlorate is bimodal. The experimental results made a definite estimation possible about the tightness of bonding between carbocation and counterion.

The investigation which constitute the present thesis deals with the propagation reaction in cationic polymerization of vinyl ethers and styrene derivatives. The cationic polymerization was apprehended as one of the electrophilic addition reactions, and the emphasis is laid on the treatment of the experimental results on the standpoint of physical organic chemistry. For the present investigation to be complete, further extensions of the studies are needed. The author, however, believes that the present studies have contributed to the elucidation of the propagation reaction in cationic polymerization to a considerable extent. The experimental results will be explained in turn in the succeeding chapters.

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PART I

CATIONIC COPOLYMERIZATION OF 2-CHLOROETHYL
VINYL ETHER WITH STYRENE DERIVATIVES

Chapter 1

Characteristics in the Copolymerization of a Vinyl Ether with Styrene Derivatives

Introduction

Styrene derivatives and vinyl ethers are representative monomers which are polymerized in cationic mechanism and have been made use of widely for the study of cationic polymerization. Many cationic copolymerizations between styrene derivatives have been carried out, and the products of monomer reactivity ratios (MRR), $r_1 \times r_2$, were found to be approximately unity.^{1,2} This holds also in the copolymerization between vinyl ethers,³⁻⁷ though data are not abundant.

On the other hand, it was found that the copolymer composition curves show an appreciable S-shape (namely, $r_1 > 1$ and $r_2 > 1$) in the copolymerization of vinyl ether with p-methoxystyrene (pMOS) and p-methylstyrene (pMS) by iodine.⁵ However, Marvel⁴ and Pepper⁸ copolymerized α -methylstyrene (α MS) or its derivatives with 2-chloroethyl vinyl ether (CEVE), finding the result that the product $r_1 \times r_2$ was not much greater than unity. Pepper suggested that the difference in the results was partly due to the difference of the polymerization conditions, e.g., the kind of catalyst.

However, the phenomenon that both r_1 and r_2 are larger than unity was observed also in the cationic copolymerization of isobutene with styrene.⁹ This suggests that the cross-propagation is difficult in the cationic copolymerization between monomers with a different type of substituent.

In this chapter, to elucidate the cause of discrepancies of the kinetic behavior between ring-substituted styrenes and α MS in cationic copolymerization with CEVE, it will be first studied whether or not a copolymer is produced in the cationic copolymerization of CEVE with styrene derivatives. After the copolymer formation is confirmed, these monomers are copolymerized in various conditions and the behavior of ring-substituted styrenes is compared with that of α MS. Further, the dependence of MRR on the kind of solvents and catalysts used will be discussed.

Experimental

pMOS and pMS were synthesized from anisole and toluene, respectively, through acetylation, reduction and dehydration procedures.¹⁰ These monomers and commercial α MS were purified by washing with 10% aqueous solution of sodium hydroxide and with water, drying over sodium sulfate and distilling two or three times over calcium hydride under reduced pressure (bp: pMOS 70°C (5 mm); pMS 51°C (15 mm); α MS 52°C (10 mm)). CEVE (Fujiwara Factory) was washed with aqueous sodium hydroxide solution and water, dried over potassium hydroxide and distilled twice over calcium hydride (bp 109°C). The purities of these monomers were found to be more than 99.9% through gas chromatography.

Toluene (Guaranteed Reagent) was washed with 10% sulfuric acid solution, water, 10% aqueous sodium hydroxide solution and water, dried over calcium chloride, and distilled firstly over sodium metal and secondly over calcium hydride (bp 111°C). Methylene chloride (Guaranteed Reagent) was washed with 10% aqueous potassium carbonate solution and then with water, dried

over calcium chloride and distilled over phosphorus pentoxide and next over calcium hydride (bp 40°C).

Boron trifluoride etherate (BF_3OEt_2) (Extra Pure) was refined by distilling commercial material (bp 125°C). Stannic chloride (SnCl_4) (Guaranteed Reagent) was distilled into a weighed small ampoule (bp 114°C). Trichloroacetic acid (TCA) (Guaranteed Reagent) was applied as the cocatalyst of SnCl_4 without further purification.

Procedures

a. Polymerization

The copolymerization was initiated by adding the catalyst solution from a syringe through a rubber stopper into an Erlenmeyer flask containing the monomer solution. After a given time, the copolymerization was stopped by adding methanol containing a small amount of diethylamine. The concentration of each residual monomer was determined by gas chromatography (Yanagimoto Model GCG 550T). Column materials and internal standards were selected so as to suit the determination of each monomer. For example, measurement conditions of CEVE-pMOS system were as follows:

Mono-mer	Carrier gas	Column material	Internal standard ^{b)}	Column temp, °C
CEVE	H_2	25% PEG ^{a)} 1500 C-22 (1.5m)	Toluene	65
pMOS	H_2	25% PEG ^{a)} 400 C-22 (0.75m)	Nitro-benzene	120

a) Poly(ethylene glycol)

b) 2 vol% of reaction solution

As it was confirmed that the consumed monomers were quantitatively converted to a methanol-insoluble copolymer, copolymer composition was determined from each monomer consumption. To avoid experimental error at determining each monomer consumption from the amount of residual monomer, total conversion was made to fall in the range of 20~30%. The arithmetically mean value of the initial and final monomer concentrations was adopted as monomer concentration to obtain a copolymer composition curve. It afforded a much better result than using the initial monomer concentration as monomer concentration. MRR were evaluated by the Fineman-Ross' method. In all cases, CEVE is taken as M_1 .

b. Molecular weight of polymer

Viscosity number (η_{sp}/C ; $C = 1.00$ g/100 ml solution) was measured in benzene solution at 30°C. Molecular weight was measured at 60°C in a cyclohexanone solution by the osmometric method.

c. Confirmation of copolymer formation

The turbidimetric titration was carried out with a Shimadzu TG21 turbidimeter. Nmr spectra of polymer were measured by a JEOL 3H-60 Spectrometer.

Results

Confirmation of Copolymer Formation

a. Viscosity and molecular weight

Methanol-insoluble polymer was produced in the copolymerization of CEVE and styrene derivatives. The yield of the methanol-insoluble polymer coincided with monomer consumption within +2% error. The dependence of viscosity number on monomer composition is shown in Figures 1 and 2. As is seen in the

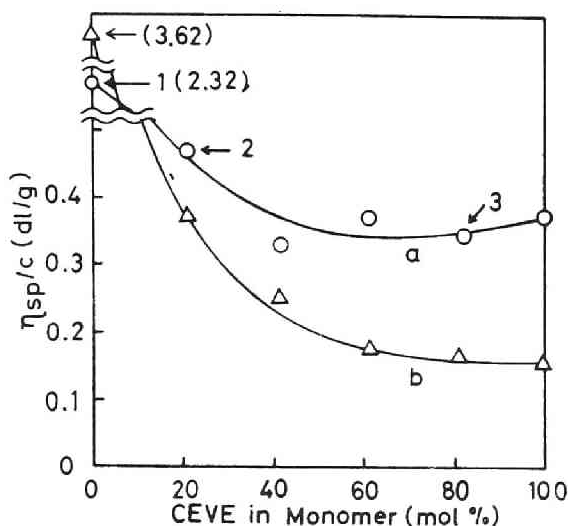


Figure 1. Relationship between monomer composition and viscosity number of CEVE-pMOS copolymers ($[M]_0$ 0.50 mol/l, solvent CH_2Cl_2 , -78°C , conversion > 80%; catalyst, a(o) BF_3OEt_2 , b(Δ) $\text{SnCl}_4\cdot\text{TCA}$). Molecular weight of polymers (the osmotic pressure method): No 1 165000, 2 49000, 3 37700.

cationic copolymerization of styrene derivatives with isobutene, the molecular weight of copolymer was smaller than that expected for homopolymers.

b. Fractionation

Fractionation of polymers obtained at high conversion was carried out to determine whether or not copolymer is formed in the polymerization of a vinyl ether and styrene derivatives. The polymer obtained in the copolymerization of CEVE with pMOS was separated with an equivolume mixture of acetone and methanol into soluble and insoluble parts at 30°C . Composition of each part is shown in Table I.

Table I. Fractionation of CEVE-pMOS polymer^{a)}

Sample No.		1	2	3	4 ^{b)}
Catalyst		BF ₃ OEt ₂	BF ₃ OEt ₂	SnCl ₄ ·TCA	—
Monomer ([CEVE] ₀ : [pMOS] ₀)		40:60	60:40	70:30	—
Fractions ^{c)} (wt %)	Soluble part	17.0	21.5	57.1	47.0
	Insoluble part	78.0	75.0	38.1	47.7
CEVE content in polymer (wt %)	Original polymer	30.4	53.5	65.3	49.2
	Soluble part	62.7	78.0	80.1	95.9
	Insoluble part	20.6	45.1	36.0	0.0

a) Polymerization conditions, [M]₀ 0.50 mol/l, Solvent: CH₂Cl₂, -78°C, Conversion 70-90%.

b) A mixture of equal weight of poly(CEVE) and poly(pMOS).

c) Loss of polymer in this procedure was ca. 5 wt %.

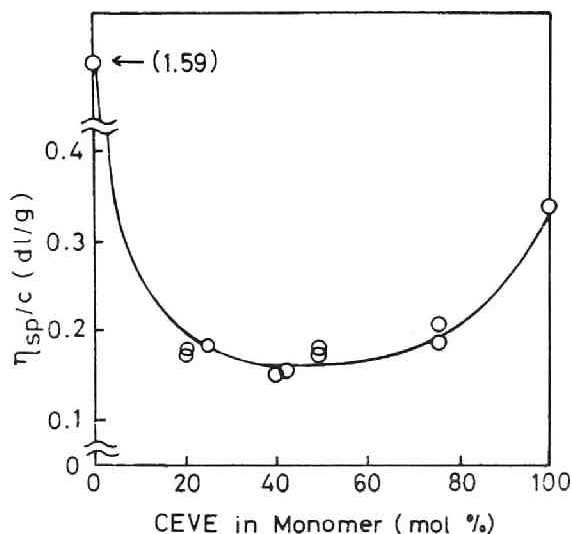


Figure 2. Relationship between monomer composition and viscosity number of CEVE- α MS copolymers ($[M]_0$ 0.50 mol/l, solvent CH_2Cl_2 , catalyst BF_3OEt_2 , -78°C , conversion > 80%).

As is seen from Table I, poly(pMOS) was scarcely dissolved in this solvent and poly(CEVE) was dissolved completely. On the other hand, both soluble and insoluble parts of the polymer obtained in the copolymerization contained both CEVE and pMOS units. Similar results were observed in the polymers obtained in the copolymerization of CEVE with α MS and of CEVE with pMS. These results show the formation of the true copolymer in the cationic copolymerization of styrene derivatives with CEVE.

c. Turbidimetric titration

The change of turbidity was measured during the course of the continuous addition of petroleum ether as nonsolvent to a benzene solution of the polymer obtained in CEVE- α MS copolymerization. As is seen from Figure 3 the curves for the polymers

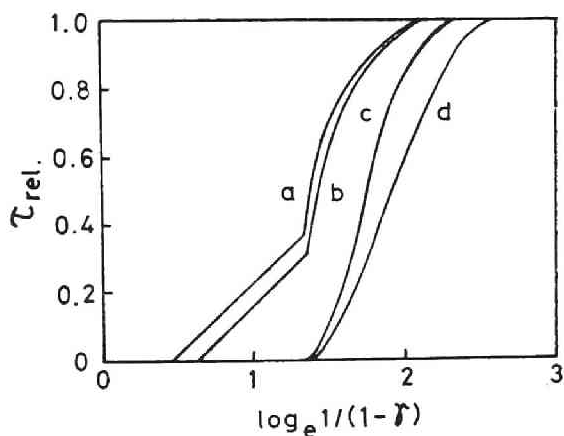


Figure 3. Turbidimetric titration curves of CEVE- α MS copolymer and the mixture of poly(CEVE) and poly(α MS) at room temperature. Polymer concn, 8 mg/dl in benzene; a, poly(CEVE)(cryst)-poly(α MS) mixture; b, poly(CEVE)(amorph)-poly(α MS) mixture; c and d, CEVE- α MS copolymer obtained in CH_2Cl_2 by $\text{SnCl}_4 \cdot \text{TCA}$ and BF_3OEt_2 , respectively.

obtained in the copolymerization were very different from those for the mixtures of homopolymers; although the copolymer solution began to be turbid at the same γ -value (the volume ratio of nonsolvent to the sum of solvent and nonsolvent) as that of poly(α MS), the change of turbidity was slow as in poly(CEVE) and the endpoint of precipitation ($\tau_{\text{rel}} = 1.0$) was observed at a higher γ -value than the mixture of homopolymer.

d. Nmr spectra

Copolymer formation was also confirmed by nmr spectroscopy. The spectra are shown in Figures 4 and 5 for CEVE- α MS and CEVE-pMS polymer, respectively. Figure 4a shows the spectrum of a mixture of poly(CEVE) and poly(α MS), which coincides well with superposition of the spectra of each homopolymer.

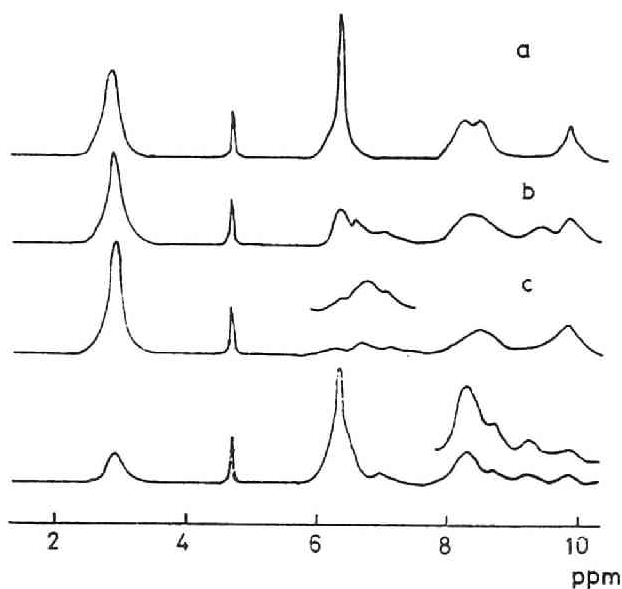


Figure 4. Nmr spectra of CEVE- α MS copolymers obtained by $\text{SnCl}_4 \cdot \text{TCA}$. (Solvent CDCl_3 , internal standard CH_2Cl_2 , polymer concn 10%, 24°C ; polymerization conditions are the same as in Figure 2). a, poly(CEVE)-poly(α MS) mixture; copolymers ($[\text{CEVE}]_0 : [\alpha\text{MS}]_0$), b, 40:60; c, 20:80; d, 80:20.

On the other hand, in CEVE- α MS copolymer many other peaks (τ 6.53, 6.91, 8.74, and 9.38) based on the difference of the neighbouring monomer unit were observed and two peaks at τ 8.22 and 8.38 became one broad peak at τ 8.30. These changes of nmr spectra suggest the formation of a true copolymer. The peaks at τ 6.53 and 6.91 are considered to be the shifted ones of alkoxy and/or methine protons through shielding by phenyl groups on either or both sides. The peak of α -methyl protons at τ 9.81 was also shifted to τ 9.38 and 8.74 by the change of the neighbouring monomer unit.

As to CEVE-pMS polymer (Figure 5c), a new peak at τ 6.60 which was absent in both homopolymers was observed. This is

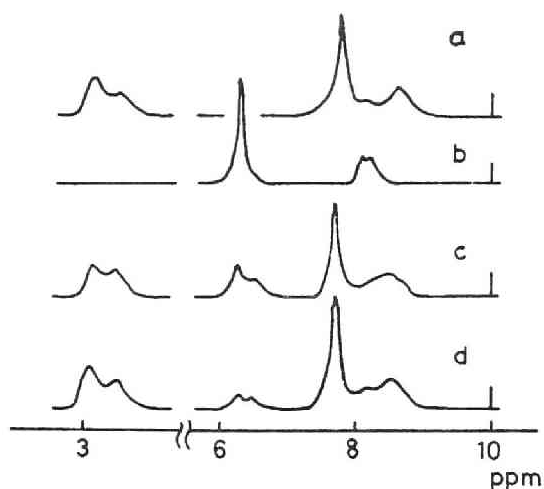


Figure 5. Nmr spectra of CEVE-pMS copolymers obtained by $\text{SnCl}_4 \cdot \text{TCA}$ (Solvent CDCl_3 , internal standard TMS, polymer concn 10%, 80°C ; polymerization conditions are the same as in Figure 2). a, poly(pMS); b, poly(CEVE); copolymers ($[\text{CEVE}]_0 : [\text{pMS}]_0$), c, 45:55; d, 15:85.

thought to appear because of shifting of alkoxy and/or methine protons due to the presence of pMS units on either or both sides. In the case of CEVE-pMS polymer, the production of a copolymer was not confirmed by nmr spectroscopy because of the overlap of peaks of alkoxy, methine and p-methoxy protons.

Relative Reactivity of CEVE and Styrene Derivatives in the Cationic Copolymerization

a. Copolymerization of CEVE with ring-substituted styrenes

Methylene chloride and toluene were used as polar and nonpolar solvents, respectively. BF_3OEt_2 and $\text{SnCl}_4 \cdot \text{TCA}$ were used as catalysts. Polymerization was carried out at -78°C . Although the reaction system contained 1-2 mmol/l of water in this case, the small amount of water did not affect MRR.

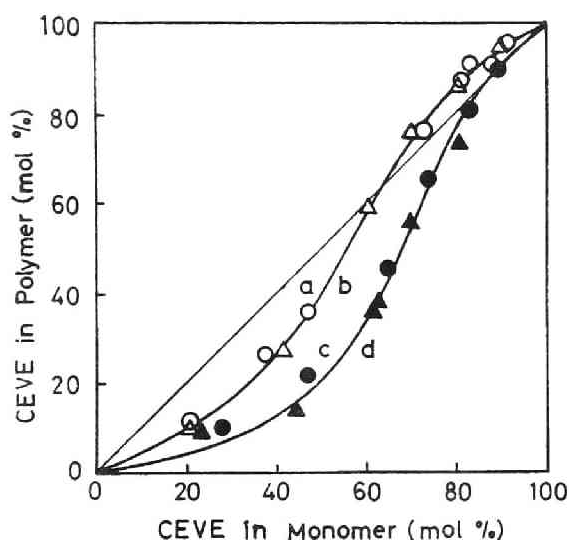


Figure 6. Copolymer composition curves of CEVE with pMOS ($[M]_0$ 0.50 mol/l, -78°C). a(o), BF_3OEt_2 , toluene; b(Δ), BF_3OEt_2 , CH_2Cl_2 ; c(\bullet), $\text{SnCl}_4\cdot\text{TCA}$, toluene; d(\blacktriangle), $\text{SnCl}_4\cdot\text{TCA}$, CH_2Cl_2 .

In Figure 6 are shown copolymer composition curves of CEVE-pMOS copolymerization. pMOS was more reactive than CEVE in equimolar copolymerization. It is also apparent that the composition curves are typically S-shaped, which means that MRR, both r_1 and r_2 , are greater than unity and that cross-propagation is difficult. Copolymer composition was unaffected by the kind of solvent, but affected by the kind of catalyst.

As is clear from Figure 7, pMS was less reactive than CEVE. In this case, also the tendency that the product $r_1 \times r_2$ exceeds unity was observed. pMS content in the copolymer was larger in methylene chloride than in toluene, and with $\text{SnCl}_4\cdot\text{TCA}$ with BF_3OEt_2 . The relative reactivity of pMS against CEVE was about half in methylene chloride with $\text{SnCl}_4\cdot\text{TCA}$, but surprisingly small in toluene with BF_3OEt_2 .

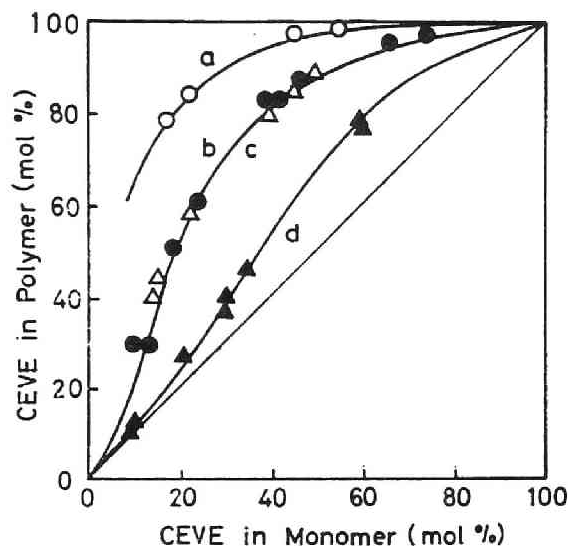


Figure 7. Copolymer composition curves of CEVE with pMS ($[M]_0$ 0.5 mol/l, -78°C). a(o), BF_3OEt_2 , toluene; b(Δ), BF_3OEt_2 , CH_2Cl_2 ; c(\bullet), $\text{SnCl}_4\cdot\text{TCA}$, toluene; d(\blacktriangle), $\text{SnCl}_4\cdot\text{TCA}$, CH_2Cl_2 .

In order to compare the reactivity of vinyl ether and styrene derivatives for a cationic reagent other than carbocation, chlorine was added to the mixture of CEVE and pMS. It was confirmed that chlorination occurred on the vinyl group under the conditions shown in Figure 8. Figure 8 shows the relationship between reactant and product compositions. The reactivity of CEVE was appreciably larger than that of pMS irrespective of reactant composition, and the composition curve in Figure 8 was not S-shaped as had been the case in copolymerization. Therefore, the S-shape in copolymerization may be due to the existence of two types of carbocation, i.e., the propagating chain ends produced from CEVE and pMS.

MRR (M_1 :CEVE) are listed in Table II. The products $r_1 \times r_2$ were 11-16 in CEVE-pMS and 3-5 in CEVE-pMS, which were clearly

Table II. Monomer reactivity ratios and a and K values calculated from eq 1 for the copolymerization of CEVE with pMOS and pMS^{a)}

Monomer	Catalyst	Solvent	r_1	r_2	$r_1 \times r_2$	a	K
CEVE-	BF_3OEt_2	Toluene	2.81 ± 0.30	4.37 ± 0.30	12.3	1.54	0.70
	"	CH_2Cl_2	3.08 ± 0.26	4.55 ± 0.35	14.0	1.58	0.65
pMOS	$\text{SnCl}_4 \cdot \text{TCA}$	Toluene	1.73 ± 0.19	6.93 ± 0.50	12.0	1.54	0.36
	"	CH_2Cl_2	1.56 ± 0.04	7.80 ± 0.20	12.2	1.58	0.29
CEVE-	BF_3OEt_2	Toluene	—	—	—	~ 1.3	~ 27
	"	CH_2Cl_2	8.80 ± 0.45	0.40 ± 0.03	3.52	1.24	7.00
pMS	$\text{SnCl}_4 \cdot \text{TCA}$	Toluene	10.1 ± 1.8	0.50 ± 0.07	5.05	1.32	7.40
	"	CH_2Cl_2	2.31 ± 0.17	1.12 ± 0.06	3.71	1.27	2.10

a) $[\text{M}]_0$ 0.50 mol/l, -78°C .

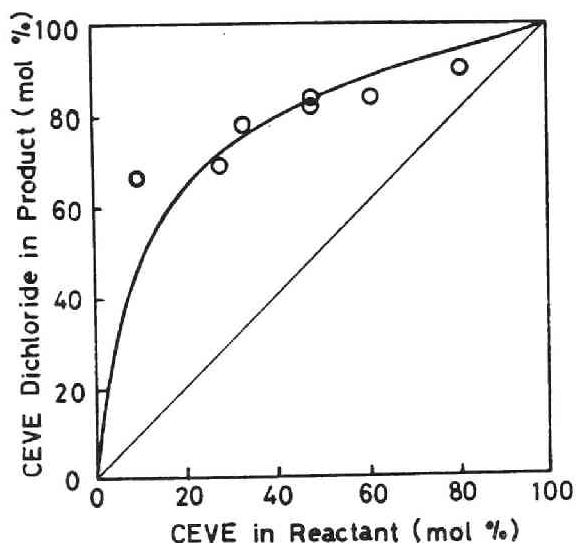


Figure 8. Relationship between the composition of initial products and that of monomers in the chlorination of CEVE-pMS mixture ($[M]_0$ 0.50 mol/l, catalyst $\text{SnCl}_4 \cdot \text{TCA}$, solvent CH_2Cl_2 , -78°C ; chlorine was bubbled slowly with oxygen into the solution).

larger than unity.

As is clear in Figure 9, the linearity between $\log ([M_1]/[M_2])$ and $\log (d[M_1]/d[M_2])$ was realized; the eq 1 proposed by O'Driscoll^{11,12} held in these systems;

$$\frac{d[M_1]}{d[M_2]} = K \left(\frac{[M_1]}{[M_2]} \right)^a \quad (1)$$

a was 1.5-1.6 in the CEVE-pMOS and 1.2-1.3 in the CEVE-pMS system. K varied significantly, depending on the type of solvent and catalyst used.

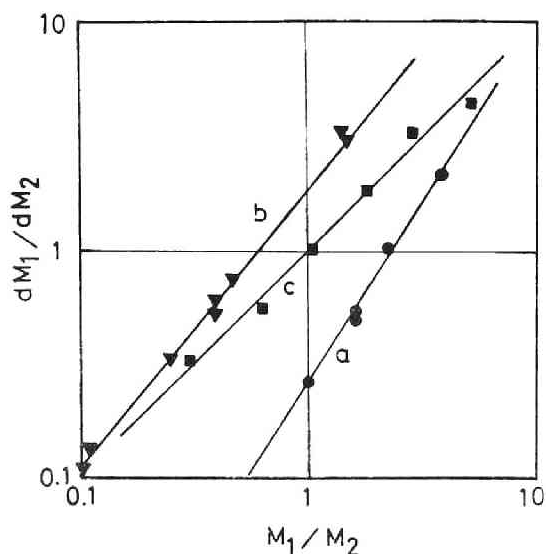


Figure 9. Relationship between $\log (M_1/M_2)$ and $\log (dM_1/dM_2)$ in the copolymerization of CEVE (M_1) with styrene derivatives (M_2) ($[M]_0$ 0.50 mol/l, catalyst $\text{SnCl}_4 \cdot \text{TCA}$, solvent CH_2Cl_2 , -78°C). a(\bullet), CEVE-pMS; b(\blacktriangledown), CEVE-pMS; c(\blacksquare), CEVE- α MS.

b. Copolymerization of CEVE with α MS

Polymerization conditions were the same as in the case of copolymerization with ring-substituted styrenes. As shown in Figure 10, the reactivity of CEVE was larger than that of α MS except the case of the $\text{SnCl}_4 \cdot \text{TCA}$ -methylene chloride system. The effects of solvent and catalyst were conspicuously great. α MS content in the copolymer was larger in methylene chloride than in toluene, and by $\text{SnCl}_4 \cdot \text{TCA}$ than by BF_3OEt_2 . These results were similar to those obtained in CEVE-pMS system.

The values of MRR determined by the Fineman-Ross' method are listed in Table III. The product $r_1 \times r_2$ was close to unity in all cases, which means that CEVE- α MS copolymerization is "ideal", that is, the relative reactivity of a monomer is

Table III. Monomer reactivity ratios and a and K values calculated from eq 1 for the copolymerization of CEVE with α MS

Catalyst	Solvent	r_1	r_2	$r_1 \times r_2$	a	K
BF_3OEt_2	Toluene	5.72 ± 0.70	0.31 ± 0.05	1.77	1.05	5.00
"	CH_2Cl_2	2.05 ± 0.33	0.68 ± 0.14	1.39	1.02	1.70
$\text{SnCl}_4 \cdot \text{TCA}$	Toluene	3.46 ± 0.25	0.46 ± 0.07	1.59	1.03	3.20
"	CH_2Cl_2	1.02 ± 0.10	1.00 ± 0.10	1.00	1.00	1.00

a) $[\text{M}]_0$ 0.50 mol/l, -78°C

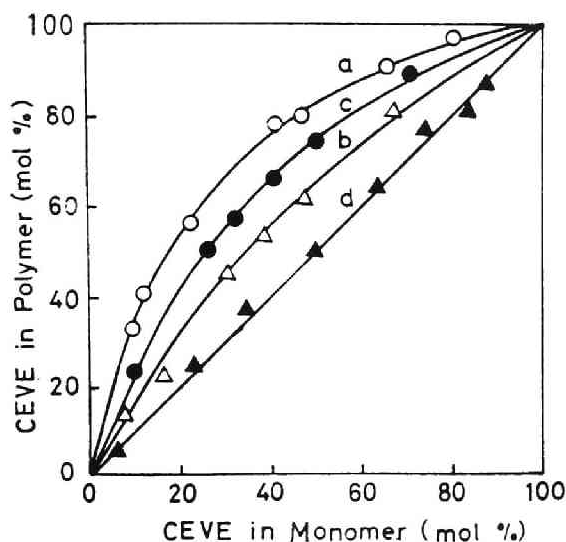


Figure 10. Copolymer composition curves of CEVE with α MS ($[M]_0$ 0.50 mol/l, -78°C) a(o), BF_3OEt_2 , toluene; b(Δ), BF_3OEt_2 , CH_2Cl_2 ; c(\bullet), $\text{SnCl}_4 \cdot \text{TCA}$, toluene; d(\blacktriangle), $\text{SnCl}_4 \cdot \text{TCA}$, CH_2Cl_2 .

independent of the type of growing carbocation. Plots of $\log (dM_1/dM_2)$ against $\log (M_1/M_2)$ gave straight lines, whose slopes were unity. a and K values are also shown in Table III.

Discussion

Formation of Copolymer

In order to study the effect of polymerization conditions on the values of MRR in cationic copolymerization, it is convenient to select a pair of monomers whose reactivities are not so different, because the alternating tendency has not been observed in ionic copolymerization.² The cationic polymerizability of vinyl ether is, in general, greater than that of styrene. Therefore, CEVE was used as vinyl ether, and

styrenes with a electron-donating group were chosen as a styrene derivative.

In the copolymerization of CEVE with these styrene derivatives, no product other than methanol-insoluble polymer was found. Formation of the copolymer was confirmed by fractionation and nmr spectra in the monomer pairs used here. Moreover, the molecular weights of the polymers produced were more than several thousands as shown in Figures 1 and 2. Therefore attention is focused on the kinetic behavior in the copolymerization.

The Difference in Behavior between Ring-substituted Styrene and α MS

The difference between ring-substituted styrenes and α MS was clearly observed in the copolymerization with CEVE under the same conditions; the product $r_1 \times r_2$ showed values larger than unity for ring-substituted styrenes, i.e. pMOS and pMS, while it proved that the values are close to unity for α MS irrespective of polymerization conditions.

On the other hand, in competitive chlorination CEVE was more reactive than pMS regardless of reactant composition. Therefore, it is concluded that the difference in selective reactivities of CEVE and pMS cations can be ascribed to the character of the carbocation itself, and not to the influence of the counter-anion and solvent.⁸ One of the reasons for the difference in the behavior between ring-substituted styrenes and α MS might be that the α MS cation is more stable than the pMOS and pMS cation. In gas phase, it was reported that the stabilization energy of the carbocation $\text{CH}_3\text{OCH}_2^+$ was almost the same as that of the isopropyl carbocation.¹³ Therefore, the stability of $(\alpha\text{MS})^+$ seems to be similar to that of $(\text{MVE})^+$, but

that of (ring-substituted styrene)⁺ will be less than that of (MVE)⁺.¹⁴

The possibility that the steric hindrance of α MS cancels the tendency of block propagation ought to be considered as another reason of randomness in CEVE- α MS copolymer. Further study and experiment will be necessary before this problem can be resolved.

The Effect of Polymerization Conditions on the Relative Reactivity of Both Monomers

The relative reactivity of the monomer can be easily estimated from MRR in the CEVE- α MS system, as $r_1 \times r_2 \approx 1$. The reactivity of CEVE is 1.7-5.0 times larger than that of α MS except the case of $\text{SnCl}_4 \cdot \text{TCA}$ -methylene chloride in which both reactivities are equal.

The relative reactivities of the monomers were changed by the type of propagating ends in the CEVE-pMS and the CEVE-pMS systems. In this case the relative reactivity can be tentatively considered as the polymer composition in the copolymerization of equimolar monomer composition. The K values in eq 1 could be used as its index. According to K values, CEVE had smaller reactivity than pMS ($K = 0.3-0.8$), and larger than pMS ($K = 2-27$).

It is well known that the kind of solvent and catalyst used affects MRR in ionic copolymerization. A tendency was recognized in the influence of the catalyst in this study: the styrene derivative content in the copolymer increased in every system irrespective of the relative reactivity of monomers, whenever $\text{SnCl}_4 \cdot \text{TCA}$ was used instead of BF_3OEt_2 . When $\text{SnCl}_4 \cdot \text{TCA}$ was used as catalyst, the relative reactivity of both monomers in the CEVE- α MS and CEVE-pMS system approached

unity, while the difference in reactivities of both monomers became rather larger in the CEVE-pMOS system. Therefore, this catalyst effect cannot be explained by the concept proposed by Tobolsky, et al.,¹⁵ that the selectivity for monomers decreases with the increase in the reactivity of growing ions. It is concluded that $\text{SnCl}_4 \cdot \text{TCA}$ is more favorable in the polymerization of styrene derivatives than BF_3OEt_2 , though the reason for this is not clear at present.

The CEVE content in the copolymers was large when a non-polar solvent was used in the copolymerization with nonpolar monomers, such as αMS and pMS . There have been two possible explanations for the influence of solvents on copolymer composition.^{15,16} One of them is "the decrease in the selectivity of the addition of an ion for each monomer with the increase in the reactivity of an ion", proposed by Tobolsky, et al.¹⁵ The other is "the selective solvation to propagating end by a polar monomer in a nonpolar solvent", proposed by Overberger, et al.¹⁶ Considering the catalyst effect, the former explanation seems to be unsuitable. It is, therefore, suggested that "selective solvation" is the predominant factor in the solvent effect in these reactions.

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Chapter 2

Temperature Dependence of Monomer Reactivity Ratios

Introduction

It was made clear in the first chapter¹ that in the cationic copolymerization of 2-chloroethyl vinyl ether (CEVE) with styrene derivatives, (1) the relative reactivity of both monomers depended largely on the kind of catalysts and solvents used, and (2) the product of the monomer reactivity ratios (MRR), $r_1 \times r_2$, was greater than unity in the copolymerization of CEVE with ring-substituted styrenes, although a copolymer was produced.

The differences in the activation parameters are obtained by studying temperature dependence of monomer reactivity ratios. In radical copolymerization, a linearity holds between $\log r$ and $1/T$ and the line passes near the origin.² This means that the activation entropies are equal at the addition of different monomers to the same propagating end, that is, the reaction mechanism is similar in both monomers.

On the other hand, plots of $\log r$ vs. $1/T$ do not pass the origin in cationic polymerization,³ although few reliable data are available. The cationic copolymerization of CEVE with α -methylstyrene (α MS) is a typical example, in which both r_1 and r_2 become far from unity as polymerization temperature is raised.⁴

In this chapter, the temperature dependence of MRR and of their product $r_1 \times r_2$ is investigated in detail in the copolymerization of CEVE with styrene derivatives to elucidate the

difference of the reaction mechanism between CEVE and styrene derivatives.

Experimental

p-Chlorostyrene (pCS) was synthesized in a similar manner to p-methoxystyrene (pMOS) and p-methylstyrene (pMS) (see the previous chapter). Isobutyl vinyl ether (IBVE) and styrene (ST) were commercially obtained and purified in the same manner as the monomers synthesized.

The purification of the other materials and the procedure of copolymerization are the same as were used in the first chapter.¹

MRR were estimated by the Fineman-Ross' method. The mean square errors of MRR were in the range of $\pm 5\%$.

Results and Discussion

Temperature Dependence of MRR

The copolymerization of CEVE with pMOS was carried out with BF_3OEt_2 in toluene at -78 , -36 and 0°C . The copolymer composition curves are shown in Figure 1. The composition curves in Figure 1 are sigmoidal and the CEVE content in copolymer increased as the temperature was raised. As the dielectric constant of toluene is almost independent of temperature, the temperature dependence observed is not based on the change in the dielectric constant of the system. The shift of the composition curves with temperature, moreover, was much larger than those in radical copolymerization of various monomers and those in cationic copolymerization of

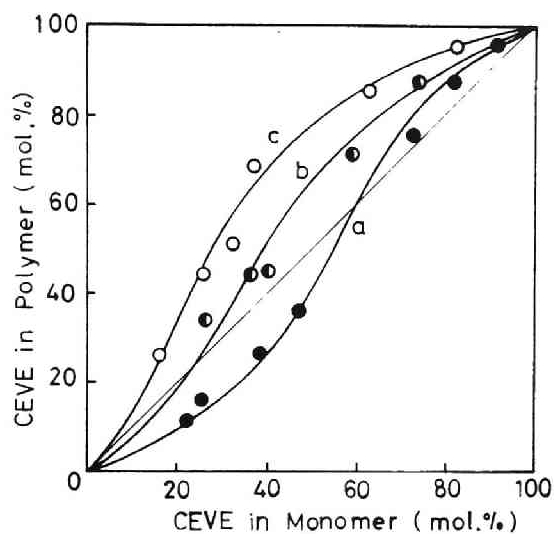


Figure 1. Composition curves for the copolymerization of CEVE with pMOS (BF_3OEt_2 , toluene, $[\text{M}]_0$ 0.5 mol/l). Temp: a(\bullet), -78°C ; b(\bullet), -36°C ; c(o), 0°C .

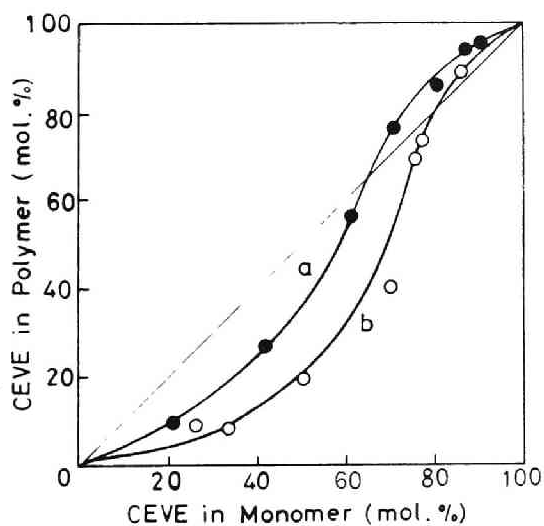


Figure 2. Composition curves for the copolymerization of CEVE with pMOS (BF_3OEt_2 , methylene chloride, $[\text{M}]_0$ 0.50 mol/l). Temp: a(\bullet), -78°C ; b(o), 0°C .

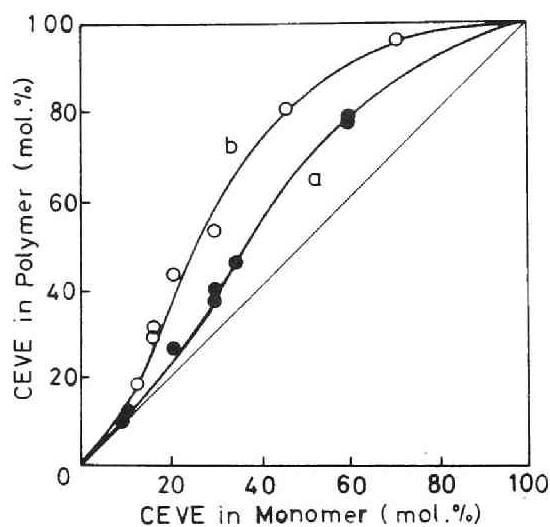


Figure 3. Composition curves for the copolymerization of CEVE with pMS ($\text{SnCl}_4 \cdot \text{TCA}$, methylene chloride, $[\text{M}]_0$ 0.50 mol/l). Temp: a(●), -78°C ; b(o), 0°C .

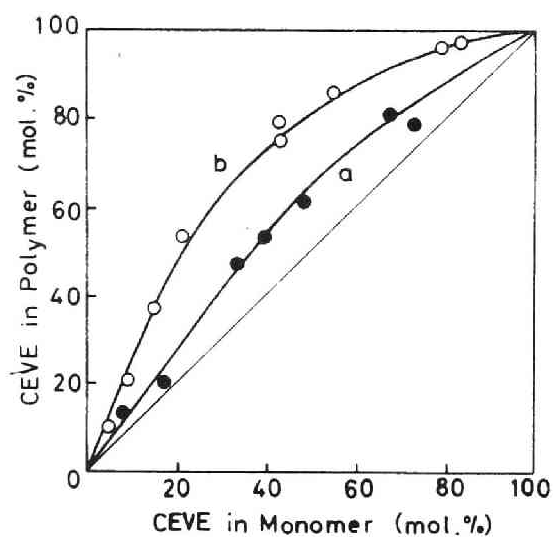


Figure 4. Composition curves for the copolymerization of CEVE with αMS (BF_3OEt_2 , methylene chloride, $[\text{M}]_0$ 0.50 mol/l at -78°C , $[\text{M}]_0$ 1.0 mol/l at -23°C). Temp: a(●), -78°C ; b(o), -23°C .

monomers having a similar substituent. When methylene chloride was used as solvent, the shift of the composition curves was also large and in the opposite direction to the case of toluene as solvent (Figure 2).

Figure 3 shows the composition curves in the copolymerization of CEVE with pMS by $\text{SnCl}_4 \cdot \text{TCA}$ in methylene chloride at -78 and 0°C . Here, $\text{SnCl}_4 \cdot \text{TCA}$ indicates that trichloroacetic acid (TCA) is used as the cocatalyst of stannic chloride in equimolar ratio. A similar change in copolymer composition with temperature was observed when toluene was used as solvent (see Table I). A characteristic of this copolymerization is that the more reactive the monomer is, the more reactive it becomes with increasing temperature. This phenomenon cannot be explained only in terms of the difference in activation energy of the propagation reaction.

The copolymerization of CEVE with αMS was carried out at -23 and -78°C , taking account of the ceiling temperature of αMS . The CEVE content in the copolymer considerably increased by increasing the polymerization temperature in the copolymerization of CEVE with αMS in methylene chloride, as shown in Figure 4. The CEVE content in the copolymer increased by increasing the polymerization temperature also in toluene, though the change was not so large as in methylene chloride (see Table I). In this case, composition curves did not show S-shape at -78°C in spite of the copolymerization of monomers with very different structure; at -23°C , however, the composition curve became slightly sigmoidal.

Copolymerization between homologues was performed to compare with the above results. The results are shown in Figure 5.

Table I. The dependence of MRR on temperature in the cationic copolymerization of vinyl ether with styrene derivatives and of homologues

No.	Monomer pair	Catalyst	Solvent	Temp, °C	r_1	r_2	$r_1 \times r_2$
1	CEVE(M ₁)-pMOS	BF ₃ OEt ₂	Toluene	0	9.32	1.55	14.4
		BF ₃ OEt ₂	Toluene	-36	5.06	2.36	11.9
		BF ₃ OEt ₂	Toluene	-78	2.81	4.37	12.3
2	CEVE(M ₁)-pMOS	BF ₃ OEt ₂	CH ₂ Cl ₂	0	1.63	9.25	15.1
		BF ₃ OEt ₂	CH ₂ Cl ₂	-78	3.08	4.55	14.0
3	CEVE(M ₁)-pMOS	SnCl ₄ ·TCA	CH ₂ Cl ₂	0	1.24	12.1	15.0
		SnCl ₄ ·TCA	CH ₂ Cl ₂	-78	1.56	7.80	12.2
4	CEVE(M ₁)-pMS	SnCl ₄ ·TCA	Toluene	0	18.2	0.40	7.28
		SnCl ₄ ·TCA	Toluene	-78	10.1	0.50	5.05
5	CEVE(M ₁)-pMS	SnCl ₄ ·TCA	CH ₂ Cl ₂	0	8.00	0.88	7.02
		SnCl ₄ ·TCA	CH ₂ Cl ₂	-78	3.31	1.12	3.70
6	CEVE(M ₁)-αMS	SnCl ₄ ·TCA	Toluene	-23	5.00	0.42	2.10
		SnCl ₄ ·TCA	Toluene	-78	3.46	0.46	1.59
7	CEVE(M ₁)-αMS	BF ₃ OEt ₂	CH ₂ Cl ₂	-23	6.02	0.42	2.53
		BF ₃ OEt ₂	CH ₂ Cl ₂	-78	2.05	0.68	1.39
8	CEVE(M ₁)-αMS	SnCl ₄ ·TCA	CH ₂ Cl ₂	-23	2.50	0.76	1.90
		SnCl ₄ ·TCA	CH ₂ Cl ₂	-78	1.02	1.00	1.02
9	ST(M ₁)-pCS	SnCl ₄ ·TCA	Toluene/	30	2.82	0.43	1.21
		SnCl ₄ ·TCA	Benzene a)	-23	2.72	0.48	1.31
10	IBVE(M ₁)-CEVE	SnCl ₄ ·TCA	Toluene	0	2.17	0.58	1.26
		SnCl ₄ ·TCA	Toluene	-78	2.17	0.58	1.26

a) Toluene: Benzene = 40:60

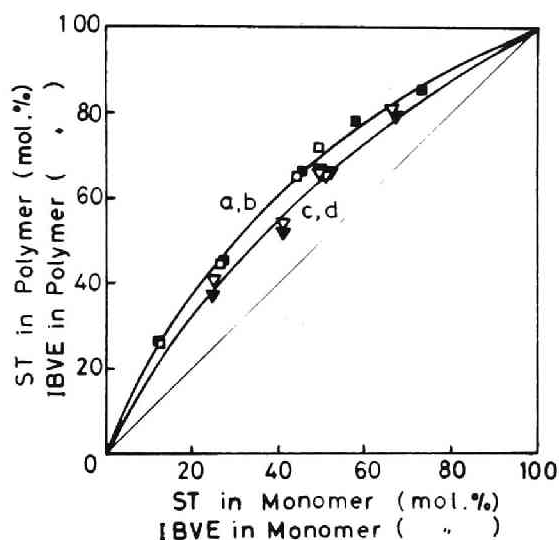


Figure 5. Composition curves for the copolymerization between homologues. ST-pCS ($\text{SnCl}_4 \cdot \text{TCA}$, toluene: benzene = 4.0:6.0, $[\text{M}]_0$ 1.0 mol/l) Temp: a(■), -23°C ; b(□), 30°C . IBVE-CEVE (BF_3OEt_2 , toluene, $[\text{M}]_0$ 0.50 mol/l), Temp: c(▼), -78°C ; d(▽), 0°C .

No difference of polymer composition was observed in the copolymerization of IBVE with CEVE by BF_3OEt_2 in toluene at -78° and 0°C . Also, there was no change in the ST-pCS system by $\text{SnCl}_4 \cdot \text{TCA}$ in a mixed solvent (toluene:benzene (volume ratio) = 40:60) at -23 and 30°C . It is concluded that in the copolymerization between homologues, copolymer composition hardly changes with temperature. It presents a striking contrast to copolymerization between monomers with different structures.

The MRR, together with their product $r_1 \times r_2$, are listed in Table I. These values were calculated on the basis of the Mayo-Lewis equation, assuming the first Markov chain model. This will be proper from the following reasons: i) the presence of cross-propagations was confirmed by nmr spectra of the

resultant polymer even in the case $r_1 \times r_2$ became fairly larger than unity, as was described in the previous chapter,¹ and ii) the linearity of the Fineman-Ross' plot held well.

In the copolymerization of CEVE (M_1) with styrene derivatives (M_2), r_1 increased and r_2 decreased by increasing the polymerization temperature in any pair of monomers by both BF_3OEt_2 and $\text{SnCl}_4 \cdot \text{TCA}$ in both toluene and methylene chloride except for the copolymerization of CEVE with pMOS. In the case of CEVE-pMOS, r_1 decreased and r_2 increased by increasing the temperature in methylene chloride. In general, it was observed that the difference in the reactivities of monomers becomes larger as the temperature is raised.

The temperature dependence of r_1 and r_2 in toluene was smaller than in methylene chloride in the CEVE-pMS and CEVE- α MS systems. r_1 and r_2 was dependent on temperature with both catalysts, BF_3OEt_2 and $\text{SnCl}_4 \cdot \text{TCA}$.

Activation parameters were calculated from the results of Table I. They are tentatively obtained from the line connecting two values observed at two different temperatures. The values are shown in Table II. The following conclusions can be obtained from Table II: (1) The values of $(\Delta H_{i1}^\ddagger - \Delta H_{i2}^\ddagger)$ have a positive sign except the CEVE-pMOS- CH_2Cl_2 system. This means that vinyl ether is less reactive in terms of enthalpy, though vinyl ether is in general more reactive than styrene derivatives. (2) Both values, $(\Delta H_{i1}^\ddagger - \Delta H_{i2}^\ddagger)$ and $(\Delta S_{i1}^\ddagger - \Delta S_{i2}^\ddagger)$, in the copolymerization of CEVE with styrene derivatives especially those of $i=1$ are considerably greater than those of the copolymerization between homologues. (3) In most cases, $(\Delta S_{i1}^\ddagger - \Delta S_{i2}^\ddagger) \times T$ is larger than $(\Delta H_{i1}^\ddagger - \Delta H_{i2}^\ddagger)$ in the copolymerization of CEVE with styrene derivatives, which indicates that

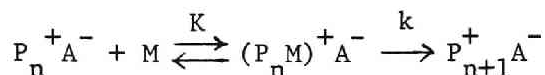
Table II. The activation parameters of MRR (from Table I)

No.	Monomer pair	Catalyst	Solvent	$\Delta H_{11}^\ddagger - \Delta H_{12}^\ddagger$	$\Delta H_{21}^\ddagger - \Delta H_{22}^\ddagger$	$\Delta S_{11}^\ddagger - \Delta S_{12}^\ddagger$	$\Delta S_{21}^\ddagger - \Delta S_{22}^\ddagger$
1	CEVE-pMOS	BF_3OEt_2	Toluene	1.9	1.6	11	4.9
2	CEVE-pMOS	BF_3OEt_2	CH_2Cl_2	-0.97	-1.1	-2.5	-8.3
3	CEVE-pMOS	$\text{SnCl}_4 \cdot \text{TCA}$	CH_2Cl_2	-0.35	-0.66	-0.78	-7.3
4	CEVE-pMS	$\text{SnCl}_4 \cdot \text{TCA}$	Toluene	0.09	0.34	9.0	3.1
5	CEVE-pMS	$\text{SnCl}_4 \cdot \text{TCA}$	CH_2Cl_2	1.4	0.38	9.1	1.6
6	CEVE- α MS	$\text{SnCl}_4 \cdot \text{TCA}$	Toluene	0.77	0.19	6.3	2.5
7	CEVE- α MS	BF_3OEt_2	CH_2Cl_2	2.1	1.0	13	5.9
8	CEVE- α MS	$\text{SnCl}_4 \cdot \text{TCA}$	CH_2Cl_2	1.9	0.53	9.5	2.6
9	St-pCS	$\text{SnCl}_4 \cdot \text{TCA}$	Toluene/ Benzene ^{a)}	0.0	0.33	2.4	2.7
10	IBVE-CEVE	$\text{SnCl}_4 \cdot \text{TCA}$	Toluene	0.0	0.0	1.5	1.1

a) Toluene: Benzene = 40:60

copolymerizations are rather entropy-controlled reactions.

These results are followed by a deduction mentioned below, on a difference in transition states of vinyl ether and styrene derivatives. It may be assumed that the propagation reaction is subdivided into two elementary reactions.⁵



Reactions in which the total number of molecules changes are usually attended by a large entropy of activation.⁶ On the other hand, the change from π -complex into σ -complex will be accompanied with an enthalpy term rather than an entropy term. Therefore, the large entropy term will mean that the first step is important in the above mechanism and the enthalpy term will depend predominantly on the second step. Consequently, it is concluded that vinyl ether suffers the first step more easily than styrene derivatives, but vice versa as to the second step. This inference will be supported by solvent and catalyst effects in the copolymerization of CEVE with styrene derivatives, as will be described in the third chapter.

The Temperature Dependence of the Product of MRR

As described in the previous section, the change in MRR with temperature suggests the difference of the transition state in addition reaction of CEVE and styrene derivatives to the carbocation. In the same way, it is expected that the temperature dependence of the product of MRR suggests the difference of behavior of the carbocation in the propagation reaction, as is shown in the following discussion.

Chūjō⁷ proposed a method for determination of the existence of the penultimate unit effect in stereospecific polymerization, which is based on the relationship between the activation free energy and polymerization temperature. The same concept will be applied to copolymerization. By plotting $\Delta\epsilon$ vs. T in eq 1, the existence of the propagating-end effect, the difference of activation enthalpy and activation entropy based on the kind of a growing chain end, can be examined, as Furukawa also suggested.⁸

$$\Delta\epsilon = -kT \ln(r_1 \times r_2) = \Delta H - T\Delta S \quad (1)$$

where $\Delta H = (\Delta H_{11}^\ddagger - \Delta H_{12}^\ddagger) - (\Delta H_{21}^\ddagger - \Delta H_{22}^\ddagger) \quad (2)$

$$\Delta S = (\Delta S_{11}^\ddagger - \Delta S_{12}^\ddagger) - (\Delta S_{21}^\ddagger - \Delta S_{22}^\ddagger) \quad (3)$$

The products of r_1 and r_2 at different temperatures are shown in Table I as to our data and in Table III as to those from other references. In the ionic copolymerizations between homologues (Table I, No. 9, 10; Table III, No. 6), the temperature dependence of $r_1 \times r_2$ is almost negligible. On the other hand, in the ionic copolymerization of the monomers with different structures (Table I, No. 1-8; Table III, No. 1-5), the product $r_1 \times r_2$ changes significantly and gets away from unity with the rise of temperature.

ΔH and ΔS are calculated and summarised in Table IV. ST-pCS systems gave similar values of ΔH and ΔS (No. B-3-6 and B-1-9 in Table IV) in spite of the different experimental conditions and workers. A good agreement was also observed in the

Table III. The products of MRR in cationic copolymerization and their temperature dependence

No.	Monomer 1	Monomer 2	Catalyst	Solvent	Temp, °C	r_1	r_2	$r_1 \times r_2$	Ref
1	IB ^{a)}	ST	AlCl ₃ (0.5%)	CH ₃ Cl	-30	2.51±0.05	1.21±0.06	3.04	9
			AlCl ₃ (0.5%)	CH ₃ Cl	-90	1.66±0.02	0.42±0.02	0.70	9
2	IB	ST	AlCl ₃ (0.14%)	CH ₃ Cl	-30	2.36±0.06	0.76±0.13	1.79	9
			AlCl ₃ (0.14%)	CH ₃ Cl	-90	1.79±0.02	0.24±0.02	0.43	9
3	ACN ^{b)}	nBVE ^{c)}	BF ₃ OEt ₂	Benzene	30	0.38±0.04	1.30±0.3	0.4-0.7	10
			BF ₃ OEt ₂	Benzene	0	0.24±0.04	4.2 ±0.8	0.7-1.4	10
			BF ₃ OEt ₂	Toluene	-20	0.14±0.03	6.0 ±1.0	0.8-1.1	10
			BF ₃ OEt ₂	Toluene	-78	0.04±0.02	~20	~0.8	10
4	CEVE	αMS	BF ₃ (CH ₃ CO ₂ H) ₂	(CH ₂ Cl) ₂	0	3.9 ±0.15	0.48±0.04	1.87	4
			BF ₃ (CH ₃ CO ₂ H) ₂	(CH ₂ Cl) ₂	-30	2.0 ±0.2	0.75±0.07	1.50	4
5	αMS	pCS	SnCl ₄	—	0	15.5±1.5	0.35±0.05	5.42	11
			SnCl ₄	—	-78	28 ±2	0.12±0.03	3.36	12
6	ST	pCS	SnCl ₄	CCl ₄	30	2.2 ±0.3	0.35±0.1	0.770	3
			SnCl ₄	CCl ₄	0	2.5 ±0.5	0.30±0.03	0.750	3
			SnCl ₄	CCl ₄	-20	2.15±0.2	0.35±0.05	0.753	3

a) IB, isobutene; b) ACN, acenaphthylene; c) nBVE, n-butyl vinyl ether.

Table IV. The activation parameters of the product of MRR in cationic copolymerization

Group	No. ^{a)}	Monomer 1	Monomer 2	Catalyst	Solvent	ΔH , kcal/mol	ΔS , e.u.
A	1-1	CEVE	pMOS	BF_3OEt_2	Toluene	~ 0.27	~ 6.3
	1-2	CEVE	pMOS	BF_3OEt_2	CH_2Cl_2	0.11	5.8
	1-3	CEVE	pMOS	$\text{SnCl}_4 \cdot \text{TCA}$	CH_2Cl_2	0.32	6.5
	1-4	CEVE	pMS	$\text{SnCl}_4 \cdot \text{TCA}$	Toluene	0.56	5.9
	1-5	CEVE	pMS	$\text{SnCl}_4 \cdot \text{TCA}$	CH_2Cl_2	0.99	7.5
	1-6	CEVE	αMS	$\text{SnCl}_4 \cdot \text{TCA}$	Toluene	0.58	3.8
	1-7	CEVE	αMS	BF_3OEt_2	CH_2Cl_2	1.1	6.8
	1-8	CEVE	αMS	$\text{SnCl}_4 \cdot \text{TCA}$	CH_2Cl_2	1.39	6.8
	3-1	IB	ST	$\text{AlCl}_3(0.5\%)$	CH_3Cl	2.2	11
	3-2	IB	ST	$\text{AlCl}_3(0.14\%)$	CH_3Cl	2.1	9.9
	3-3	ACN	nBVE	BF_3OEt_2	Benzene or Toluene	~ -1.6	~ -7.9
	3-4	CEVE	αMS	$\text{BF}_3(\text{CH}_3\text{CO}_2\text{H})_2$	$(\text{CH}_2\text{Cl})_2$	0.96	4.8
	3-5	αMS	pCS	SnCl_4	—	~ 0.63	5.9
B	1-9	ST	pCS	$\text{SnCl}_4 \cdot \text{TCA}$	Toluene/ Benzene ^{b)}	~ -0.3	~ -0.3
	1-10	IBVE	CEVE	BF_3OEt_2	Toluene	0	0.46
	3-6	ST	pCS	SnCl_4	CCl_4	~ 0.12	~ -0.20

a) Numbers refer to those of Table I and III.

b) Toluene: Benzene = 40:60.

CEVE- α MS system (see No. B-3-4 and B-1-7 in Table IV).

$\Delta\epsilon$ is, in general, independent of T in radical copolymerization. This means that the propagating-end effect at the addition of both monomers is hardly controlled by the entropy term, that is, there is no difference of activation entropy due to the kind of growing chain end.

In the cationic copolymerization between homologues, $r_1 \times r_2$ is constant and close to unity irrespective of temperature. This means that ΔH and ΔS approximately equal zero. As is seen from Table IV, both ΔH and ΔS of group B are very small. Therefore, there is no difference in reactivities of both propagating ends for monomers. This agrees with the absence of the alternating tendency in cationic copolymerization.

In the cationic copolymerizations of the monomers with different structures, ΔH and ΔS are usually different from zero (Table IV, Group A). Moreover, $T\Delta S$ is nearly equal to ΔH or is larger than ΔH in contrast to radical copolymerization. This means that the difference in reactivities of both propagating ends for monomers is controlled rather by the entropy term than by the enthalpy term. The great value of ΔS suggests the difference in the correlation between the propagating end, the counterion and monomer in the transition state.

In the previous chapter,¹ the results that the product $r_1 \times r_2$ was about unity in the copolymerization of CEVE with α MS at -78°C was explained by the similar stability of two carbocations formed from both monomers. It may be, however, only fortuitous that $r_1 \times r_2$ is close to unity in the copolymerization of CEVE with α MS at -78°C . For, ΔH and ΔS have considerably larger values than those of the copolymerization between homologues.

As is seen from Group A in Table IV, ΔH has a positive sign, and $T\Delta S$ has generally a larger positive value than ΔH in the copolymerization of monomers with different structures. This means that the higher the temperature, the higher the blocking tendency. The tendency is very conspicuous and consistent in all systems.

The above-mentioned difference in reactivities of both propagating ends for monomers is summarized as follows:

Mechanism	Structure of monomers	ΔH	ΔS	$\Delta \epsilon$
Radical	—	≥ 0	~ 0	≥ 0
Cationic	Similar	~ 0	~ 0	~ 0
	Dissimilar	> 0	> 0	≥ 0

It is concluded that vinyl ether is less reactive in terms of enthalpy and more reactive in terms of entropy than styrene derivatives; this suggests the difference between the transition state of the addition of vinyl ether and that of styrene derivatives. Further, in general, r_1 , r_2 and $r_1 \times r_2$ change remarkably with temperature in the cationic copolymerization of monomers with different structures. This means that the reaction is controlled not only by the enthalpy term but also by the entropy term, and indicates that the complex formation is not negligible and that three elements, a propagating carbocation, a counterion and a monomer are concerned at the transition state.

The above discussion was based on the assumption that the copolymer composition was controlled by a polymer chain end, because the presence of the penultimate effect could not be confirmed. Further studies on the sequence distribution in copolymers are necessary in order to elucidate the details of the mechanism.

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Chapter 3

Effects of Solvent and Catalyst on Relative Reactivity

Introduction

In the previous chapters,^{1,2} it was shown that monomer reactivity ratios (MRR) were very sensitive to reaction conditions in the cationic polymerization of 2-chloroethyl vinyl ether (CEVE) with styrene derivatives, and the temperature dependence of MRR was investigated in detail.

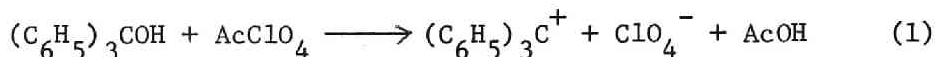
A remarkable change in MRR is often caused by varying reaction conditions in anionic polymerization, for example, in the copolymerization of styrene with methyl methacrylate³ or isoprene.⁴ On the other hand, there are relatively few cationic copolymerizations in which MRR greatly depends on reaction conditions. The copolymerization of isobutene with styrene derivatives⁵ is one of the examples.

The studies on the dependence of relative reactivity of two compounds on reaction conditions, such as solvent and catalyst, often contribute to the elucidation of reaction mechanism. Therefore, it will be very interesting to investigate the influences of solvent and catalyst on the relative reactivity of two monomer in the cationic copolymerization of CEVE with styrene derivatives. In this chapter, the changes in the relative reactivity of CEVE and styrene derivatives with the type of catalyst and solvent will be discussed.

Experimental

Aluminum bromide (Guaranteed Reagent) was purified by sublimation under reduced pressure.

Acetyl perchlorate (AcClO_4) was prepared as follows: silver perchlorate (Guaranteed Reagent) was dried at 70° for two hours under a vacuum. 100 cc of elaborately purified methylene chloride and 0.010 mole of freshly distilled acetyl chloride were successively added to 0.011 mole of the silver perchlorate. The mixture was stirred overnight at room temperature in the dark. The formed supernatant acetyl perchlorate solution was preserved in ampoules at -20° . The concentration was determined spectroscopically on the basis of reaction (1) [$(\text{C}_6\text{H}_5)_3\text{C}^+$: $\epsilon_{435} = 3.69 \times 10^4$ l/mole] :



Nitroethane (Guaranteed Reagent) was washed with aqueous solution containing 25g each of sodium bicarbonate and sodium bisulfite per liter, 5% sulfuric acid solution, and water, successively. Then, it was dried over calcium chloride and twice distilled over calcium hydride.

The synthesis and purification of the other materials and the copolymerization procedure are the same as those described in the previous chapters.^{1,2} The relative reactivity in copolymerization was determined by measuring the residual monomers in the reaction system by gas chromatography.

Results

The copolymerization of CEVE with styrene derivatives was carried out at -78°C in equimolar monomer ratio (total monomer concentration: 0.50 mol/l). AlBr_3 , stannic chloride with equimolar trichloroacetic acid ($\text{SnCl}_4 \cdot \text{TCA}$), boron trifluoride diethyl etherate (BF_3OEt_2) and AcClO_4 were used as catalysts. Toluene was used as a nonpolar solvent, and methylene chloride and nitroethane as polar solvents.

Table I shows the relative reactivity of CEVE against styrene derivatives. The relative reactivity was obtained from the ratio of initial slopes in time-conversion curves of both monomers. The values in Table I are the averages of three or four experimental values, and the residual error was less than 10%.

In the copolymerization of CEVE with p-methoxystyrene (pMOS) in toluene and methylene chloride, the relative reactivity of pMOS decreased in the following order of catalysts: $\text{AlBr}_3 > \text{SnCl}_4 \cdot \text{TCA} > \text{BF}_3\text{OEt}_2 > \text{AcClO}_4$. An opposite tendency, however, was observed in nitroethane solvent. When BF_3OEt_2 and AcClO_4 were used as catalysts, the relative reactivity of CEVE decreased with increase in the dielectric constant of a solvent.

In the copolymerization of CEVE with p-methylstyrene (pMS), the relative reactivity in toluene changed from 8.5 to > 40 when AcClO_4 was used instead of AlBr_3 . The relative reactivity of the toluene- AcClO_4 system which was determined by gas chromatography, was confirmed by the fact that no pMS unit was obtained at low conversion. On the other hand, it decreased from 1.8 to 0.43 in nitroethane. The relative reactivity of CEVE decreased with an increase in the polarity of solvent,

Table I. Relative reactivity of CEVE against styrene derivatives in the equimolar copolymerization ($[M]_0 = 0.50 \text{ mol/l}$, -78°C)

Monomer	Solvent	Catalyst			
		AlBr_3	$\text{SnCl}_4 \cdot \text{TCA}$	$\text{BF}_3 \cdot \text{OEt}_2$	AcClO_4
CEVE-pMOS	Toluene	0.23 ₇	0.33 ₃	0.68 ₇	1.7 ₂
	Methylene chloride	0.20 ₂	0.29 ₀	0.64 ₇	0.91 ₆
	Nitroethane	0.51 ₅	0.50 ₄	0.17 ₁	0.24 ₂
CEVE-pMS	Toluene	8.4 ₈	7.4 ₀	~ 27	> 40
	Methylene chloride	2.1 ₀	2.1 ₀	7.0 ₀	9.1 ₀
	Nitroethane	1.7 ₈	1.6 ₃	2.9 ₇	0.42 ₉
CEVE- α MS	Toluene	2.5 ₇	3.1 ₇	4.9 ₉	18.0
	Methylene chloride	0.97 ₁	1.0 ₀	1.7 ₈	4.0 ₃
	Nitroethane	1.7 ₄	1.6 ₇	2.0 ₉	0.54 ₆

Table II. Relative reactivity of ST against pMS in the equimolar copolymerization ($[M]_0$ 1.00 mol /l, 30°C)

Solvent	AlBr ₃	SnCl ₄ ·TCA	BF ₃ OEt ₂	AcClO ₄
Benzene	0.79 ₀	0.34 ₅	0.43 ₂	—
Methylene chloride	0.52 ₂	0.41 ₀	0.43 ₀	0.35 ₁
Nitroethane	0.36 ₈	0.38 ₀	0.33 ₉	0.38 ₆

and a large change in MRR was observed in copolymerizations using BF₃OEt₂ and AcClO₄. It is surprising that the relative reactivity changed from 40 to 0.43, that is, by a hundred times, with change in solvent from toluene to nitroethane, when AcClO₄ was used as a catalyst.

The results of the copolymerization of CEVE with α -methylstyrene (α MS) showed tendencies similar to the CEVE-pMS and CEVE-pMS systems. That is, the relative reactivity of CEVE against styrene derivatives increased greatly in toluene and methylene chloride, when AcClO₄ was used as catalyst. However, the difference in the relative reactivity with the kind of catalyst was small in nitroethane. When BF₃OEt₂ and AcClO₄ were used as catalysts, the relative reactivity of CEVE decreased with increasing solvent polarity.

The copolymerizations of styrene (ST) with pMS and of isobutyl vinyl ether (IBVE) with CEVE were carried out under similar conditions in order to know whether such large effects of catalyst and solvent are observed in the copolymerization between monomers of similar structure.

Copolymerization of ST with pMS was carried out at 30°C and the total monomer concentration was 1.00 mol/l. As shown

Table III. Relative reactivity of IBVE against CEVE in the equimolar copolymerization ($[M]_0$ 0.50 mol /l, -78°C)

Solvent	AlBr_3	$\text{SnCl}_4 \cdot \text{TCA}$	$\text{BF}_3 \cdot \text{OEt}_2$	AcClO_4
Toluene	1.6 ₄	1.6 ₇	1.8 ₆	1.8 ₉
Methylene chloride	2.5 ₇	2.6 ₈	1.9 ₀	2.2 ₇
Nitroethane	1.4 ₆	1.5 ₇	1.3 ₆	1.5 ₅

in Table II, the relative reactivity of ST, taking that of pMS as unity, was in the range of 0.34~0.52 except for the case of the AlBr_3 -benzene system. Tobolsky and his coworkers reported that the ST content became larger with a stronger catalyst and in a less polar solvent such as the SbCl_5 -toluene system.⁷ Substantially, as is seen from Table II, the relative reactivity of ST with pMS did not vary significantly with the kind of catalyst and solvent.

Copolymerization of IBVE with CEVE was performed at -78°C and the total monomer concentration was 0.50 mol/l. As shown in Table III, large effects of solvent and catalyst were not observed in the copolymerization of IBVE with CEVE. The values are 2.6 and 2.7 in the CH_2Cl_2 - AlBr_3 and CH_2Cl_2 - $\text{SnCl}_4 \cdot \text{TCA}$ systems. In other cases the values are 1.4~2.3. This change is much smaller than in the CEVE-styrene derivative systems.

Discussion

In Table IV the changes in the relative reactivity of styrene derivatives against CEVE with different solvents and catalysts are

Table IV. Summary of the changes in the relative reactivity of styrene derivatives against CEVE in copolymerization

			Strength or polarity	Relative reactivity against CEVE		
				pMS	pMS	αMS
a	Polar solvent	Catalyst	↑	→	→	→
b	Nonpolar solvent	Catalyst	↑	↑	↑	↑
c	Strong catalyst	Solvent	↑	↘	↗	↘
d	Weak catalyst	Solvent	↑	↑	↑	↑

summarized. The relative reactivity of styrene derivatives did not change significantly in a polar solvent such as nitroethane (a in Table IV).

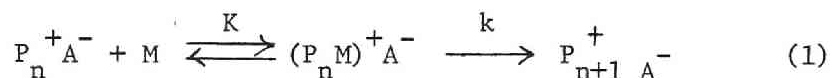
The order, $\text{AlBr}_3 > \text{SnCl}_4 > \text{BF}_3\text{OEt}_2$, in the catalyst activity was observed in cationic polymerization of isobutene⁸ and other monomers. Further, H_0 (Hammett acidity function) of HBF_4 was found to be -16.6, while the H_0 of anhydrous protonic acid is from -11 to -10⁹. Therefore, the following order of catalyst activity is settled: $\text{AlBr}_3 > \text{SnCl}_4 \cdot \text{TCA} > \text{BF}_3\text{OEt}_2 > \text{AcClO}_4$ although it is well known that the order of catalytic activity of metal halides varies with particular reactions.

As shown in b of Table IV, the relative reactivity of styrene derivatives increased with the catalyst strength in a less polar solvent such as methylene chloride and toluene. The relative reactivity of styrene derivatives increased and then decreased with the polarity of solvent using strong

catalysts such as AlBr_3 and $\text{SnCl}_4 \cdot \text{TCA}$ (c of Table IV). It increased consistently with increases in the polarity when weak catalysts such as AcClO_4 were used (d of Table IV).

Higashimura¹⁰ accounted for the changes of MRR in the cationic copolymerization of styrene with p-methylstyrene⁷ in terms of two quantum-mechanically calculated energies, E^π and E_{rs} , which, respectively, are measures of complex formation between monomer and carbocation, and resonance stabilization of the transition state as a result of incipient bond formation.

The above-mentioned results may also be discussed in a similar manner. The propagation reaction of cationic polymerization was assumed to divide into two elementary reactions¹¹:



The propagation rate constant k_p can be given as in eq 2, supposing $K \ll 1$.

$$k_p = \frac{kK}{K[M] + 1} \approx kK \quad (2)$$

K and k are related to the energy terms E^π and E_{rs} ,

$$\ln K = (\text{const})' - E^\pi/RT \quad (3)$$

$$\ln k = (\text{const})'' - E_{rs}/RT \quad (4)$$

where E^π is the energy contributing to stabilization in the formation of π -complex between propagating ion and monomer, and E_{rs} is the stabilization energy accompanying bond formation

between carbon r of a propagating ion and carbon s of a monomer. Accordingly, the partial activation energy due to π -electrons of propagating reaction, E^* , is related to E^π and E_{rs} :

$$E^* = (\text{const}) - (E^\pi + E_{rs}) \quad (5)$$

E_{rs} and E^π are dependent on the coulomb integral, α_r , on an atom r. α_r is dominated by a charge on carbon r, so that it will vary with the distances of carbon r from a counterion and from a basic solvent. This concept leads to

$$\alpha_r = \alpha - \delta\beta - \delta'\beta \quad (6)$$

$$\delta = \text{const} \cdot \frac{Q_r e^2}{R} \quad (7)$$

$$\delta' = \text{const} \cdot \frac{Q_r \cdot Q_N e^2}{R'} \quad (8)$$

where α is the coulomb integral for chain end cation unperturbed by a counterion or solvent; δ and δ' are measures of the influence of the electrostatic field of the counterion and solvent, respectively, on the atom r; Q_r and Q_N are the net charges on the carbon r of chain end and on the nucleophilic site of a solvent, respectively, and R and R' are the distances between the carbon r and the counterion or solvent, respectively. δ decreases as the dielectric constant of a solvent or the strength of a catalyst increases. δ' increases with the increase in the nucleophilicity of solvents. As E_{rs} and E^π are functions of relative δ and δ' values, they can be calculated as described by Higashimura.¹⁰ E_{rs} and E^π were proved to become larger as

Table V. The dependence of δ , δ' , and E^* on the kind of solvents and catalysts

Fixed	Strength or polarity	δ	δ'	E^π, E_{rs}	E^*
a Polar solvent	Catalyst \uparrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow
b Nonpolar solvent	Catalyst \uparrow	\searrow	\rightarrow	\nearrow	\searrow
c Strong catalyst	Solvent \uparrow	\searrow	\nearrow	\curvearrowright	\curvearrowright
d Weak catalyst	Solvent \uparrow	\searrow	\nearrow	\nearrow	\searrow

δ decreased. Similar behavior is assumed also with regard to δ' .

The change in rate of homopolymerization to be expected is shown in Table V. Here, toluene, methylene chloride, and nitroethane were used as solvents; the last has not only a large dielectric constant but also a considerable nucleophilicity. As a distinct example of the influence of nucleophilicity, neither monomer was consumed in the copolymerization of CEVE with styrene derivatives in diethyl ether because of a large nucleophilicity of the solvent.¹² Such a change in reactivity, controlled not only by solvent polarity but also by solvent nucleophilicity, is also seen in the polymerization of N-phenylethyl-eneimine.¹³

The change of relative reactivity of CEVE against styrene derivatives will be decided by the relative importance of the change in E^π or E_{rs} with polymerization conditions in the polymerization of these monomers. As vinyl ethers have a

Table VI. Expected and observed dependence of relative reactivity of styrene derivatives on the kind of solvents and catalysts

Fixed	Strength or polarity	δ	δ'	Relative reactivity of styrene derivatives	
				Expected	Observed
a Polar solvent	Catalyst \uparrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow
b Nonpolar solvent	Catalyst \uparrow	\searrow	\rightarrow	\nearrow	\nearrow
c Strong catalyst	Solvent \uparrow	\searrow	\nearrow	\curvearrowright	*
d Weak catalyst	solvent \uparrow	\searrow	\nearrow	\nearrow	\nearrow

* Complicated but not a large change (cf. Tables I and IV).

larger solvating power than styrene derivatives,¹⁴ it is supposed that the reactivity of vinyl ethers is hardly affected by the kind of solvent and catalyst used. Therefore, the change of relative reactivities in the copolymerization of CEVE with styrene derivatives should be mainly controlled by the styrene derivatives. This means that the difference of E^π or E_{rs} (ΔE^π or ΔE_{rs}) in the copolymerization of styrene derivatives with CEVE will change similarly to that of the styrene derivatives.

On the basis of this concept, the expected and observed changes in relative reactivity are shown in Table VI. The agreement is good. For example, when a weak catalyst was used, the relative reactivity of styrene derivatives increased consistently with increasing polarity of solvent, as δ decreased sharply with the solvent polarity (d in Table VI). When a

strong catalyst was used, however, the influence of a solvent was more complex (c in Table VI) because the counterion produced from a strong catalyst may easily dissociate. A nucleophilic solvent may easily solvate a dissociated ion and decrease the reactivity of a growing chain.

It is concluded that the rate-determining steps in the propagation reaction of vinyl ether and styrene derivatives are not the same, mainly owing to the difference in the solvating power of monomers, and that in consequence the relative reactivities of these monomers are much affected by the kind of catalyst and solvent.

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PART II

SUBSTITUENT EFFECT IN CATIONIC POLYMERIZATION OF VINYL ETHERS AND STYRENES

—4—

Chapter 4

Effect of β -Substituents on Reactivity

Introduction

It is well known that the β -alkyl-substituted vinyl ethers and styrenes are polymerizable by cationic mechanism. This presents a striking contrast to the reluctance of α,β -disubstituted ethylenes in radical polymerization.¹ The following knowledges have been obtained so far concerning to the reactivity of β -methyl-substituted vinyl monomers in cationic polymerization:²⁻⁶ a) a propenyl ether is more reactive than the corresponding vinyl ether in general, but β -methylstyrene is less reactive than styrene, b) the cis isomer of a propenyl ether is more reactive than the trans isomer, irrespective of the nature of the propagating end, while trans- β -methylstyrene is more reactive than cis- β -methylstyrene in the copolymerization with styrene, but the cis isomer is more reactive than the trans isomer in the mutual copolymerization of geometric isomers of anethole.

In this chapter, the influences of solvent, catalyst and temperature on the relative reactivity of β -methyl-substituted vinyl ethers and styrenes were examined in detail. One of the purposes in this investigation is to know how the effects of solvent, catalyst and temperature come out in the polymerization reaction of α,β -disubstituted ethylenes. And, another purpose is, if possible, to find a more general tendency as to

the relative reactivity of α,β -disubstituted ethylenes.

Experimental

Isobutyl propenyl ether (IBPE) was synthesized by elimination of alcohol from the pertinent acetal which was prepared from isobutyl alcohol and propionaldehyde.² The geometric isomers were separated by fractional distillation through a spinning band column of over 70 theoretical plates. The isomeric purities of cis-IBPE and trans-IBPE were 98.5 and 99.1 %, respectively. cis-Anethole was synthesized by decarboxylation of p-methoxy- β -methylcinnamic acid which was prepared from p-anisaldehyde by Perkin reaction.^{7,8} The cis isomer was separated from the trans isomer by fractional distillation. The composition of anethole after the distillation was 91 % cis isomer and 9 % trans isomer (bp 98-102°C (16mm)). p-Methoxystyrene (pMOS) was synthesized as described before.⁹ Isobutyl vinyl ether (IBVE) and trans-anethole was commercially obtained. The purifications of these monomers, solvents and catalysts are the same as described in previous chapters.

The detail of the copolymerization procedure is also described in a previous chapter.⁹ Monomer reactivity ratios were calculated by means of the Ezrielev's method,¹⁰ an improved Fineman-Ross' method. The calculation was carried out on a FACOM 230-60 computer at the Data Processing Center of Kyoto University.

Results

Solvent Effect

Toluene and nitroethane were used as nonpolar and polar

solvents, respectively. Figure 1 shows the composition curves in the copolymerization of IBVE with IBPE catalyzed by BF_3OEt_2 at -78°C . It is clear from Figure 1 that cis-IBPE has a greater

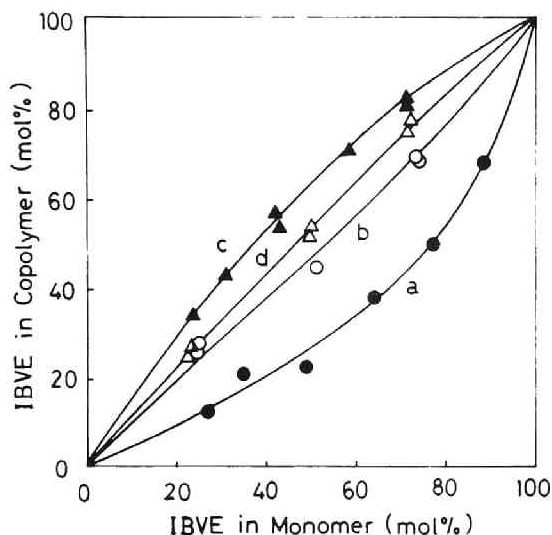


Figure 1. Solvent effect on copolymer composition of IBVE with IBPE by BF_3OEt_2 at -78°C . cis-IBPE: a(●) toluene, b(○) nitroethane; trans-IBPE: c(▲) toluene, d(△) nitroethane.

reactivity than IBVE, but trans-IBPE is rather less reactive than IBVE in toluene. When nitroethane is used as solvent, the relative reactivity of cis-IBPE decreases and that of trans-IBPE increases. Thus, the reactivities of cis-IBPE, IBVE and trans-IBPE become appreciably close each other. The monomer reactivity ratios of these systems are summarized in Table I. As M_1 is IBVE in the copolymerization, $1/r_1$ means the relative reactivity of IBPE to IBVE for the propagating end consisting of IBVE unit. The same conclusions as mentioned above can be drawn from the

Table I. Monomer reactivity ratios in the copolymerization of
IBVE with IBPE

No.	Monomers		Solvent	Catalyst	Temp, °C	r_1	r_2	$1/r_1$
	M_1	M_2						
1	IBVE	cis-IBPE	Toluene	BF_3OEt_2	-78	0.21 ± 0.05	2.38 ± 0.26	4.76
2	"	"	Nitroethane	BF_3OEt_2	-78	0.67 ± 0.06	0.78 ± 0.05	1.49
3	"	"	Toluene	$\text{SnCl}_4 \cdot \text{TCA}$	-78	0.70 ± 0.16	1.47 ± 0.31	1.43
4	"	"	Toluene	BF_3OEt_2	0	0.30 ± 0.04	0.76 ± 0.08	3.33
5	IBVE	trans-IBPE	Toluene	BF_3OEt_2	-78	1.72 ± 0.11	0.60 ± 0.04	0.58
6	"	"	Nitroethane	BF_3OEt_2	-78	1.36 ± 0.10	1.01 ± 0.08	0.74
7	"	"	Toluene	$\text{SnCl}_4 \cdot \text{TCA}$	-78	1.51 ± 0.15	0.47 ± 0.06	0.66
8	"	"	Toluene	BF_3OEt_2	0	1.84 ± 0.10	0.44 ± 0.05	0.54

values of $1/r_1$ in Table I.

Figure 2 shows the results about solvent effect in the copolymerization of pMOS with anethole. As is clear from

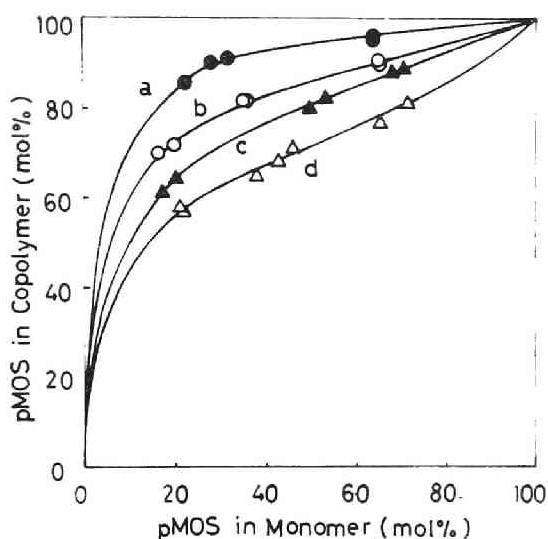


Figure 2. Solvent effect on copolymer composition of pMOS with anethole by BF_3OEt_2 at -78°C . cis-anethole: a(●) toluene, b(o) nitroethane; trans-anethole: c(▲) toluene, d(△) nitroethane.

Figure 2, trans-anethole is more reactive than cis-anethole in the copolymerization with pMOS. Further, when nitroethane is used as solvent instead of toluene, the relative reactivities of both cis- and trans-anetholes increase and approach that of pMOS. The monomer reactivity ratios in the copolymerization of pMOS (M_1) and anethole (M_2) are listed in Table II. r_2 is nearly zero, which indicates that pMOS has a much larger reactivity than anethole for anethole propagating end. This does not mean $k_{22} = 0$

Table II. Monomer reactivity ratios in the copolymerization of pMOS with anethole

No.	Monomers		Solvent	Catalyst	Temp, °C	r_1	r_2	$1/r_1$
	M_1	M_2						
1	pMOS	cis-An ^{a)}	Toluene	BF ₃ OEt ₂	-78	9.03±0.65	0.00±0.02	0.11
2	"	"	Nitroethane	BF ₃ OEt ₂	-78	4.42±0.27	0.00±0.02	0.23
3	"	"	Toluene	SnCl ₄ ·TCA	-78	3.60±0.23	0.00±0.02	0.28
4	"	"	Toluene	BF ₃ OEt ₂	0	7.73±0.57	0.00±0.03	0.13
5	IBVE	trans-An	Toluene	BF ₃ OEt ₂	-78	3.17±0.05	0.00±0.01	0.32
6	"	"	Nitroethane	BF ₃ OEt ₂	-78	1.40±0.10	0.00±0.03	0.71
7	"	"	Toluene	SnCl ₄ ·TCA	-78	1.71±0.09	0.01±0.02	0.58
8	"	"	Toluene	BF ₃ OEt ₂	0	2.11±0.24	0.00±0.07	0.47

a) An: anethole.

because anethole can produce a homopolymer. $1/r_1$ in the copolymerization of pMOS with cis- and trans-anetholes in toluene are 0.11 and 0.32, respectively, which are considerably small than unity. The relative reactivities of cis- and trans-anetholes to pMOS increases by about two times using nitroethane as solvent.

Catalyst Effect

In a polar solvent the influence of a counterion on the propagation reaction is estimated to be small on account of large solvation effect. Therefore, catalyst effect was investigated in toluene. Stannic chloride with equimolar trichloroacetic acid as cocatalyst ($\text{SnCl}_4 \cdot \text{TCA}$) was used as a catalyst to compare with BF_3OEt_2 . The former catalyst is, in general, accepted to be stronger than the latter. As shown in Figure 3, the relative reactivity of cis-IBPE to IBVE decreased by use of $\text{SnCl}_4 \cdot \text{TCA}$ as catalyst. $1/r_1$ reduced to one third (see Table I). On the contrary, the relative reactivity of trans-IBPE to IBVE was almost unaffected by the kind of catalysts.

Figure 4 shows the catalyst effect in the copolymerization of pMOS with anethole. In both cis- and trans-anetholes, the relative reactivity of anethole catalyzed by $\text{SnCl}_4 \cdot \text{TCA}$ is higher than that catalyzed by BF_3OEt_2 by 2-3 times. It is interesting that the direction of the change in relative reactivity of anethole with the kind of catalysts is opposite to that of IBPE.

Temperature Effect

To gain an insight into the temperature dependence of relative reactivity, the copolymerization was carried out at

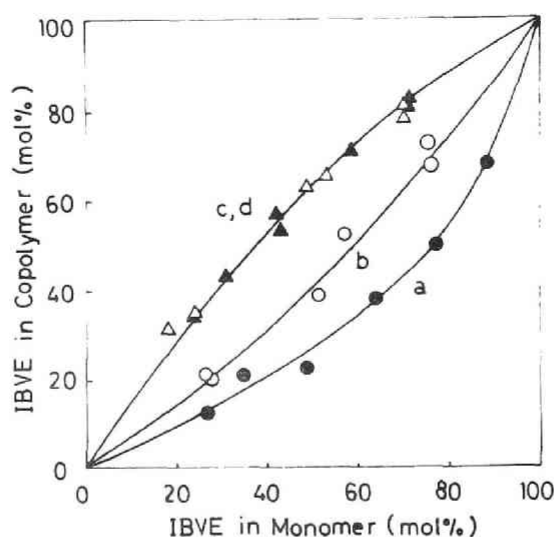


Figure 3. Catalyst effect on copolymer composition of IBVE with IBPE in toluene at -78°C . cis-IBPE: a(●) BF_3OEt_2 , b(o) $\text{SnCl}_4\cdot\text{TCA}$; trans-IBPE: c(▲) BF_3OEt_2 , d(Δ) $\text{SnCl}_4\cdot\text{TCA}$.

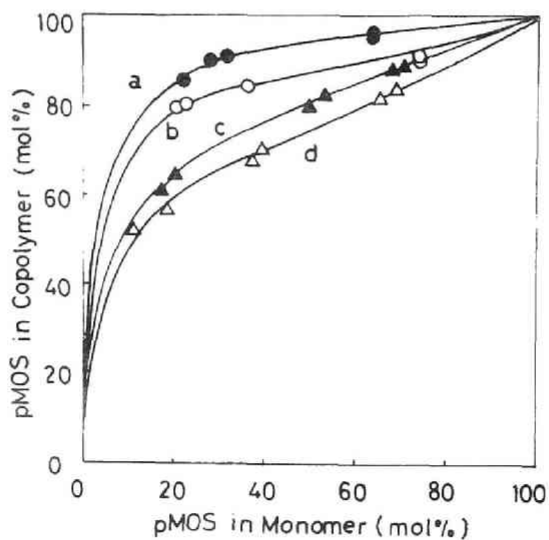


Figure 4. Catalyst effect on copolymer composition of pMOS with anethole in toluene at -78°C . cis-anethole: a(●) BF_3OEt_2 , b(o) $\text{SnCl}_4\cdot\text{TCA}$; trans-anethole: c(▲) BF_3OEt_2 , d(Δ) $\text{SnCl}_4\cdot\text{TCA}$.

-78° and 0°C in toluene using BF_3OEt_2 as catalyst. The results are shown in Figures 5 and 6. A distinct temperature dependence

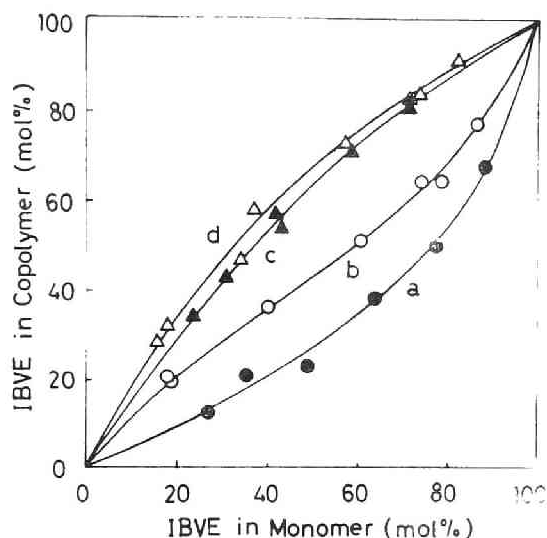


Figure 5. Temperature dependence of copolymer composition of IBVE with IBPE in toluene by BF_3OEt_2 . cis-IBPE: a(●) -78°C , b(o) 0°C ; trans-IBPE: c(▲) -78°C , d(Δ) 0°C .

of relative reactivity was observed in the copolymerization of IBVE with cis-IBPE. $1/r_1$ changes from 4.76 to 3.53. In the case of trans-IBPE, the relative reactivity of IBPE increased slightly with the increase in polymerization temperature. Concerning to anethole (Figure 6), the influence of temperature is considerably small in both geometrical isomers. In both cases, the reactivity of anetholes seems to increase slightly at a higher temperature.

The results obtained in this investigation is summarized as follows: a) The order of reactivities in the vinyl ethers is

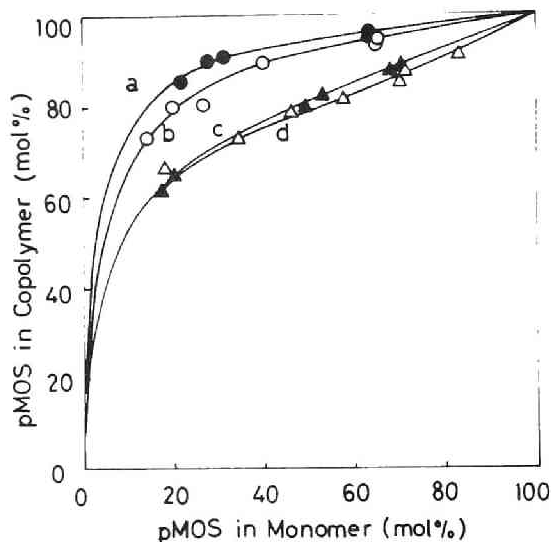


Figure 6. Temperature dependence of copolymer composition of pMOS with anethole in toluene by BF_3OEt_2 . cis-anethole: a(●) -78°C , b(o) 0°C ; trans-anethole: c(▲) -78°C , d(Δ) 0°C .

cis-IBPE > IBVE > trans-IBPE. When solvent polarity increases, catalyst strength increases, or temperature is elevated, then the relative reactivity of cis-IBPE decreases considerably and so approached to that of IBVE. However, the same changes in polymerization conditions gave rise to small and equivocal changes in relative reactivity of trans-IBPE. b) The reactivities of the p-methoxystyrenes lay in the order pMOS > trans-anethole > cis-anethole. As solvent polarity and catalyst strength increase or temperature is raised, the relative reactivities of both cis- and trans-anethole to pMOS increase.

Discussion

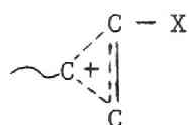
The influence of a polar substituent in the para position

of phenyl group is usually explicable by electronic effect. Meanwhile, the introduction of an alkyl group into β -position of a vinyl group has not only electronic but also steric influence on a reaction. Cis and trans isomers derived by β -methyl substitution may suffer similar changes electronically from unsubstituted one, but steric states are appreciably different each other. While trans isomer is affected usually only by intermolecular steric hindrance on a reaction, neither inter- nor intra-molecular steric hindrance can be disregarded in cis isomer.

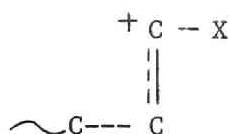
When a more polar solvent is used, following influences are expected to turn out in cationic polymerization: a) a propagating ion pair becomes looser, and in consequence more reactive, so that the selectivity of the ion pair for reactants reduces, b) as the charge of the carbocation is liable to localize on the α -carbon, the influence of a β -substituent becomes small, c) a monomer which has a large intermolecular steric hindrance becomes more reactive owing to the looseness of the ion pair, and d) the reactivity of a more basic monomer reduces relatively. It is, however, not necessary to take account of (d) in the present system because the basicities of β -substituted and unsubstituted ones are little different. This presents a contrast to the copolymerization of a vinyl ether and a styrene derivative in which (d) is a main factor determining the relative reactivity. When a stronger catalyst is applied, a), b) and c) are anticipated. A higher temperature may give rise to following consequences: a) as the reactivity of a propagating ion pair increases, the selectivity of ion pair decreases, and b) the reactivity of a monomer which is less reactive in terms of enthalpy is enhanced.

The results of the present study is summarized as follows: when the copolymerization of IBVE with IBPE or of pMOS with anethole is carried out in a more polar solvent, by a stronger catalyst or at a higher temperature, the relative reactivities of the two monomers approach each other, in general. The following two explanations seem probable for this trend.

One of the interpretations is "reduction of selectivity", that is, the reactivity of ion pair increase with the change in reaction conditions as described above, its selectivity for reactants reduces, and consequently the relative reactivity approaches unity. Another is represented as "localization of charge"; a carbocation whose charge is localized on the α -carbon is favored in a polar solvent and/or with a strong catalyst, so that the transition state of propagation reaction is changed, more or less, in the direction from model I to model II. The



(I)



(II)

influence of a β -substituent seems to be small in model II compared with model I. Thus, the reactivity of a β -substituted monomer approaches to that of the corresponding unsubstituted monomer.

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Chapter 5

Effect of α -Substituents on Reactivity

Introduction

In general, α,β -disubstituted ethylenes are impossible to polymerize under radical mechanism, but are often capable of cationic polymerization. The influence of a substituent at β -position of vinyl monomers on cationic polymerizability has been studied, and the transition state of propagation reaction has been discussed in detail on the basis of the electronic and steric effects of a substituent.^{1,2}

As for α,α -disubstituted ethylenes, isobutene and α -methylstyrene have great cationic polymerizabilities, so that the kinetics of polymerization of these monomers has been studied widely. However, there have been few works in which the cationic polymerizability of α,α -disubstituted ethylenes has been compared with that of monosubstituted ethylenes. Therefore, it seems important at this stage to investigate how the introduction of α -substituents affects reactivity, in order to obtain more information about the mechanism of cationic polymerization.

In this chapter, the reactivity of several α -substituted vinyl ethers and styrenes in cationic homopolymerization and copolymerization will be dealt with. The observed reactivities are discussed on the basis of the electronic and steric factors of α -substituents. Moreover the differences in the α -methyl-substituent effect in cationic polymerization of vinyl ether and

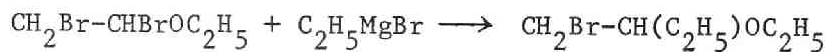
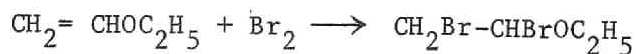
styrene, and the differences in the α -methyl-substituent effect in several electrophilic addition reactions are also discussed.

Experimental

Materials

Ethyl α -methylvinyl ether (ethyl isopropenyl ether; E α MVE) was prepared by the dealcoholation of acetone diethyl ketal under the catalysis of sulfanilic acid. Acetone diethyl ketal was prepared by Hurd's method.³ bp 61°C, $n_D^{20} = 1.5301$, $d_D^{20} = 0.950$ (lit bp 61.9°C, $n_D^{20} = 1.3927$ ⁴).

Ethyl α -ethylvinyl ether (E α EVE) was synthesized according to the following formulae:



α,β -Dibromoethyl vinyl ether was prepared by adding equimolar bromine to ethyl vinyl ether at 0°C slowly so that the temperature did not rise. The second and third steps were carried out substantially in the manner of Lauer and Spielman.⁵ The dehydrobromination by reflux of isopropanol solution was much more effective than that by distillation over potassium hydroxide. bp 86°C, $n_D^{20} = 1.3996$, $d_4^{20} = 0.7808$ (lit bp 85-87°C, $n_D^{24.5} = 1.4011$ ⁵).

Ethyl α -phenylvinyl ether (E α PVE) was prepared in a similar manner to ethyl α -ethylvinyl ether. bp 69°C (8mm), $n_D^{20} = 1.5301$, $d_4^{20} = 0.950$ (lit bp 96-98°C (19mm), $n_D^{26} = 1.5271$ ⁵).

The synthesis of α -ethylstyrene (α ES) was as follows: at first 2-phenyl-n-butanol was synthesized by reducing 2-phenyl-n-

butyric acid with lithium aluminum hydride. Then it was dehydrated by the catalytic action of a 10 : 1 mixture of sodium and potassium hydroxides and the distillate at 70°C (15mm) was collected. bp 67°C (15mm), $n_D^{20} = 1.5285$, $d_4^{20} = 0.9579$, $\lambda_{\max} 241\text{m}\mu$, $\epsilon_{\max} 1.03 \times 10^4$ (lit bp 85-86°C (30mm), $n_D^{26.5} = 1.5260^6$).

1,1-Diphenylethylene (DPE) was synthesized from phenylmagnesium bromide and acetophenone, modifying the Allen's method.⁷ bp 120°C (5mm), $n_D^{20} = 1.6099$, $d_4^{20} = 1.0115$ (lit bp 123-125°C (5mm), $n_D^{20} = 1.6085^7$).

The synthesized and commercial monomers (ethyl vinyl ether:EVE; styrene:ST) were refined, care being taken to remove water. The catalysts and solvents used were purified as described elsewhere.^{8,9}

Procedures

The polymerization was carried out in an Erlenmeyer flask under a dry nitrogen atmosphere. Feeding of materials was carried out with hypodermic syringes. The polymerization rate and relative reactivity were determined by measuring the consumption of monomers by gas chromatography. Nmr spectra of polymers were measured in 10 % solution in carbon tetrachloride at ambient temperature. Monomer reactivity ratios were calculated by the Ezrielev's method.¹⁰

Results

Homopolymerizability

a. α -Substituted vinyl ethers

Ethyl α -methylvinyl ether can be polymerized easily to

produce a methanol-insoluble polymer at -78°C in toluene or methylene chloride by various catalysts. Figure 1 shows

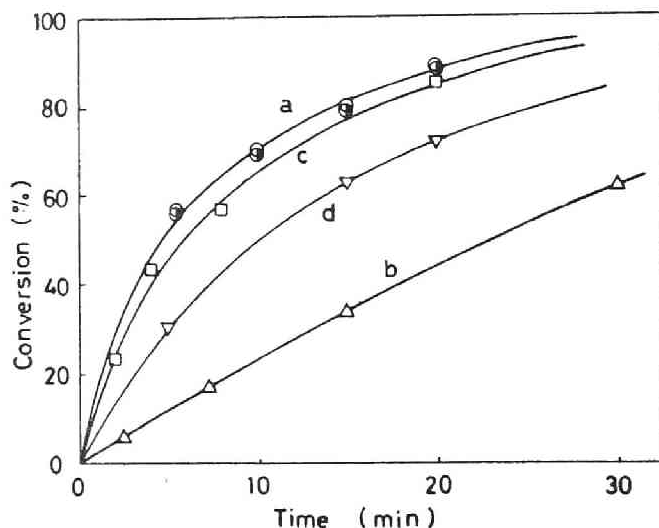


Figure 1. Time-conversion curves in the polymerization of E α MVE at -78°C ($[\text{M}]_0$ 1.0 mol/l, $[\text{C}]_0$ 0.50 mmol/l). Solvent and catalyst; a(\circ), toluene, I_2 ; b(Δ), toluene, FeCl_3 ; c(\square), toluene, AcClO_4 ; d(∇), CH_2Cl_2 , I_2 (\bullet), Yield of methanol-insoluble polymer).

time-conversion curves in the polymerization with several catalysts. It was confirmed that the consumed monomer is converted quantitatively to a methanol-insoluble polymer. As the α -unsubstituted vinyl ether polymerizes at 30°C at a similar rate, ethyl α -methylvinyl ether was estimated to have a large reactivity. The viscosity numbers of the polymers obtained were very different: 0.1-0.9 according to the change of catalyst, with those of the ferric chloride catalyst being especially large (Figure 2). All the polymers proved to have an exclusively

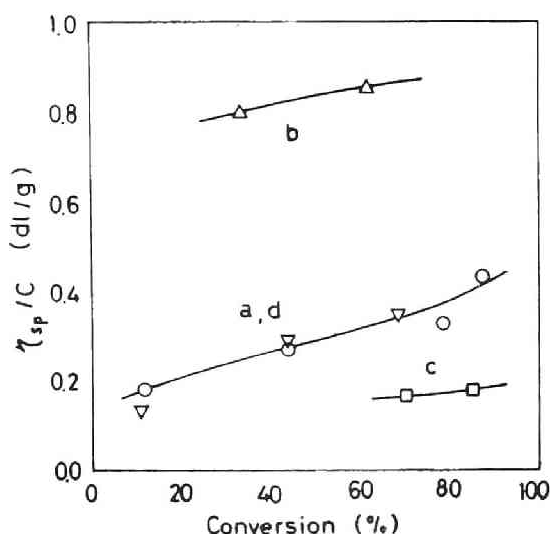


Figure 2. Viscosity numbers of poly(EoMVE) obtained under various conditions (Polymerization conditions: $[M]_0$ 1.0 mol/l, $[C]_0$ 0.50 mmol/l, -78°C ; Conditions of viscosity measurement: concn 1.00g/dl, benzene, 30°C). Solvent and catalyst: a(o), toluene, I_2 ; b(Δ), toluene, FeCl_3 ; c(\square), toluene, AcClO_4 ; d(∇), CH_2Cl_2 , I_2 .

syndiotactic structure independent of the kind of catalyst and solvent, which is in fair accord with the reported structure of poly(methyl α -methylvinyl ether).¹¹ This result means that the steric structure of the polymer is not controlled by a counterion existing near the propagating end but controlled by the substituents of the monomer and propagating end, that is, substituent-controlled and not counterion-controlled.

Next, the influence of bulkier substituents than the methyl group was studied. Ethyl α -ethylvinyl ether reacts at -78°C in toluene at a much smaller rate than that of ethyl α -methylvinyl ether and does not form a methanol-insoluble polymer (Table I). It is reported that ethyl α -ethoxyvinyl ether (ketene diethyl acetal) reacts, by acids as weak as cadmium and zinc chlorides

Table I. Possibility of homopolymerization of
several α,α -disubstituted monomers

Monomer	Catalyst	[Cat], mmol/l	Time, hr	Conversion, %	
				Monomer consumption	MeOH-insol polymer
E α EVE	I ₂	1.0	1	0	0
	BF ₃ OEt ₂	10	0.5	40	0
α ES	AcClO ₄	5.0	20	0	0
	BF ₃ OEt ₂	10	20	0	0
E α PVE	AcClO ₄	5.0	20	0	0
	BF ₃ OEt ₂	10	20	0	0

Polymerization conditions; Solvent, toluene;
-78°C; [M]₀, 1.0 mol/l.

into a glassy polymer.¹² Ethyl α -phenylvinyl ether is not consumed at all at -78°C in toluene with various catalysts though the system is colored red (Table I). The color seems to be due to a stable carbocation formed from the monomer.

b. α -Substituted styrenes

As is well known, α -methylstyrene gives easily a methanol-insoluble polymer with acidic catalysts. α -Ethylstyrene was not consumed under mild conditions as shown in Table I. Its dimerization, however, takes place without difficulty as reported by Overberger.⁶ α -Ethoxystyrene (ethyl α -phenylvinyl ether) has already been mentioned in the above section. Evans has investigated the dimerization of 1,1-diphenylethylene which does not polymerize.¹³ These results demonstrate that α -substituted styrenes are, in general, difficult to polymerize by an acidic catalyst owing to steric hindrance.

Copolymerizability

a. α -Methyl substitution

In Figure 3 are shown the copolymer composition curves in the copolymerization of ethyl vinyl ether (M_1) with ethyl α -methylvinyl ether (M_2) and of styrene (M_1) with α -methylstyrene (M_2). In both cases α -substituted monomers have a fairly larger reactivity than the unsubstituted ones. $1/r_1$ of the vinyl ether system, the relative reactivity of α -methylvinyl ether to vinyl ether for the vinyl ether propagating end, is about 8 (see Table II). $1/r_1$ of the styrene system is about 4, and smaller than that of the vinyl ether system.

b. α -Ethyl substitution

Figure 4 shows the composition curves in the copolymeriza-

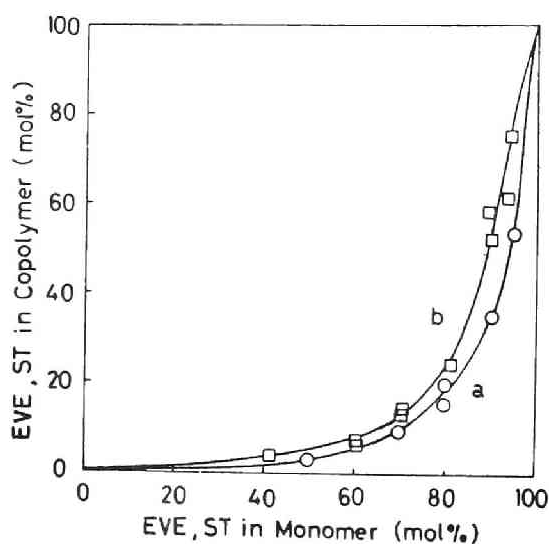


Figure 3. α -Methyl substitution effect in the copolymerization in methylene chloride at -78°C , $[M]_0$ 0.50 mol/l. a(o), EVE-E α MVE(BF_3OEt_2); b(□), ST- α MS ($\text{SnCl}_4 \cdot \text{TCA}$).

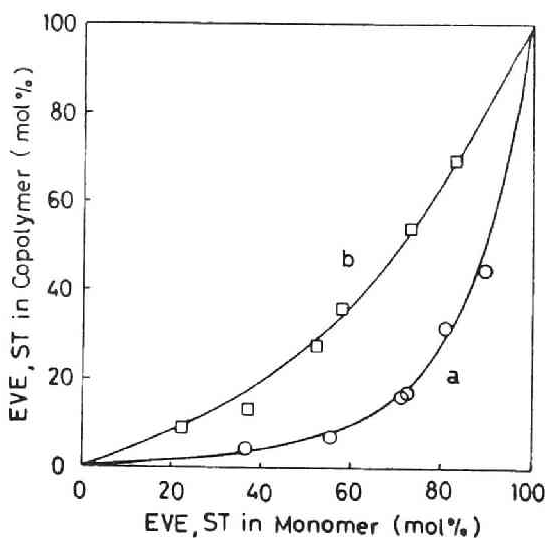


Figure 4. α -Ethyl substitution effect in the copolymerization in methylene chloride at -78°C , $[M]_0$ 3.0 mol/l. a(o), EVE-E α EVE(BF_3OEt_2); b(□), ST- α ES ($\text{SnCl}_4 \cdot \text{TCA}$).

Table II. Monomer reactivity ratios in the copolymerizations between α -substituted and unsubstituted monomers

Monomer 1	Monomer 2	Catalyst	Solvent	Temp, °C	r_1	r_2	$1/r_1$	$r_1 \times r_2$
EVE	E α MVE	BF ₃ OEt ₂	CH ₂ Cl ₂	-78	0.13 \pm 0.04	29.3 \pm 3.5	7.7	3.8
EVE	E α EVE	"	"	"	0.11 \pm 0.05	13.8 \pm 1.6	9.0	1.5
EVE	E α PVE	"	Toluene	"	($r_1 = r_1'$) \sim 0.5 ^{a)}	(r_2') \sim 20 ^{a)}	\sim 2	
ST	α MS	SnCl ₄ ·TCA	CH ₂ Cl ₂	"	0.25 \pm 0.08	20.6 \pm 3.5	4.0	5.2
ST	α ES	"	"	"	0.53 \pm 0.17	3.2 \pm 0.5	1.9	1.7
ST	DPE	"	"	"	0.88 \pm 0.08	0.03 \pm 0.03	1.1	0.0

a) The penultimate model and further $r_2 = 0$, $r_1 = r_1'$ assumed.

tion of α -substituted (M_2) with unsubstituted (M_1) monomers, and the monomer reactivity ratios are given in Table II. In the copolymerization of ethyl vinyl ether (M_1) and ethyl α -ethylvinyl ether (M_2), r_1 is 0.11 and r_2 13.8. The reactivity is not so elevated by α -ethyl substitution as by α -methyl substitution. This may be due to the steric effect of the ethyl group because the ethyl group is more electron-donating and so enhances reactivity electronically more than the methyl group. In the copolymerization of styrene with α -ethylstyrene in methylene chloride, dimerization also proceeds during polymerization when the α -ethylstyrene content is large in the feed. Accordingly, r_2 is only apparent, since M_2 does not homopolymerize. On the other hand, $1/r_1$ conforms to the copolymerization theory, and the value of $1/r_1$ indicates that α -ethyl substitution brings about an increase in the reactivity only by two times.

c. α -Phenyl substitution

In the copolymerization of α -phenyl-substituted monomers with unsubstituted ones, unusual copolymer composition curves are obtained owing to the bulkiness of the substituents (see Figure 5). Copolymer of ethyl vinyl ether and ethyl α -phenylvinyl ether always contains more than 33 mol % ethyl vinyl ether, as was expected by Lüssi.¹⁴ When the vinyl ether content is less than 20 mol % in feed, the copolymer formed is expected to have a regular structure of $\langle M_1M_2M_2 \rangle_n$ sequence. The monomer reactivity ratios were obtained by a curve-fitting method assuming the penultimate model and $r_2 = 0$, $r_1 = r_1'$. The system was colored red by adding catalyst and discolored as the polymerization was stopped with methanol.

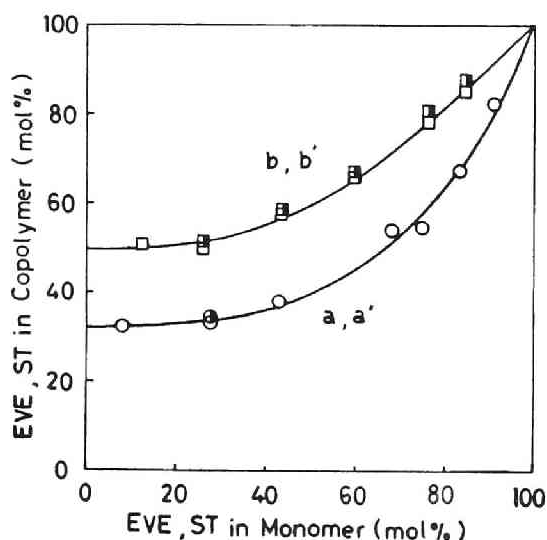


Figure 5. α -Phenyl substitution effect in the copolymerization at -78°C , $[M]_0$ 3.0 mol/l. a(o), EVE-E α PVE (toluene, AcClO_4); b(\square), ST-DPE (CH_2Cl_2 , $\text{SnCl}_4 \cdot \text{TCA}$) (a'(\bullet), b'(\blacksquare): Copolymer composition analysis by nmr).

In the case of styrene-diphenylethylene copolymerization, the steric effect becomes more outstanding and 1:1 alternating copolymer is obtained when the styrene content is less than 20 mole % in feed. The copolymer compositions were determined by nmr spectroscopy. The value of $1/r_1$ is about unity, which means the relative reactivity of both monomers for styrene propagating end is about equal. The polymerization system was colored red.

Discussion

The above-mentioned results are summarized in Table III. Ethyl α -methylvinyl and α -ethoxyvinyl ethers homopolymerize, but α -ethyl- and α -phenyl-substituted vinyl ethers do not. α -Substituted styrenes, except α -methylstyrene, cannot produce

Table III. The cationic polymerizability of α -substituted vinyl ether and styrene relative to unsubstituted monomers

α -Substituent	Vinyl Ether		Styrene	
	Homopoly- merizability	Copoly- ^{a)} merizability	Homopoly- merizability	Copoly- ^{a)} merizability
CH ₃	>>1	7.7	>>1	4.0
C ₂ H ₅	0	9.0	0	1.9
OC ₂ H ₅	>>1 ^{b)}	>>1 ^{b)}	0	>>1
C ₆ H ₅	0	\sim 2	0	1.1

a) $1/r_1$ (M_1 : unsubstituted monomer) is used as the measure.

b) Expected from the data in ref 12.

homopolymers. These results mean that steric effect is very important in the cationic homopolymerization of α,α -disubstituted ethylenes. The extent of steric hindrance by the α -substituents is greater in styrene than in vinyl ether, as is clear from the homopolymerization of α -ethoxy-substituted monomers and from copolymerization of α -phenyl-substituted monomers (see Table III).

The relative reactivity of the α -substituted vinyl monomer to the corresponding α -unsubstituted vinyl monomer is, as shown in Table III, made greater by methyl and ethoxy substitution, but not so great by ethyl and phenyl substitution. The increase in reactivity by substitution might be expected to lie in the order of $C_2H_5O > C_6H_5 > CH_3 \sim C_2H_5$ electronically, but the actual reactivity becomes complex according to the superposition of steric effect.

When the methyl group is introduced at β -position the reactivity in cationic polymerization of vinyl ether becomes 1-4 times greater and that of styrene about 0.1-0.7 times. Comparing this with the results for α -methyl substitution, it is clear that α -substitution for the methyl group is more effective to the enhancement of reactivity than β -substitution in cationic polymerization.

In Table IV are listed the changes in reactivity with α -methyl substitution of vinyl ether and styrene in several reactions. Protonation reactions (hydrolysis, hydration and alcoholations) are accelerated by 10^2 - 10^4 times by substituting for the methyl group at α -carbon. On the contrary, the acceleration is no more than 3-13 times in the bromination and cationic polymerization. Further, the equilibrium constants of complex formation with silver ion or iodine molecule hardly changes or becomes smaller when the methyl group is substituted for. This tendency suggests that the smaller and the harder the electrophilic reagent, the greater the relative reactivity of the α -methyl-substituted reactant. This is explained as follows: by substituting α -proton for the methyl group, the electron density on β -carbon in a double bond increases and that on α -carbon decreases, that is, the introduction of the methyl group induces an imbalance of electron density distribution in the double bond. Then the olefin will be more susceptible to attack by a hard acid such as proton, since the acid will act selectively only on the β -carbon of a double bond. The effect will not be so great in the case of a soft acid like silver ion or iodine because the acid attacks both carbons of a double bond at an early stage of the rate-determining step. It can be said that the substituent effect in

Table IV. α -Methyl substitution effect on the reactivity of vinyl ether and styrene in various cationic and related reactions

Reactant	Reaction	Ratio ^{a)} of k or K	Reaction conditions	Ref
	Hydrolysis	1.9×10^4	25°C , HClO_4 , dioxan- H_2O (80:20)	15
	"	1.3×10^4	25°C , HCl , dioxan- H_2O (80:20)	16
Ethyl	Bromination	3.0	0°C , CCl_4	17
Vinyl	"	3.2	0°C , CH_2Cl_2	17
Ether	Polymerization	9.1	-78°C , BF_3OEt_2 , CH_2Cl_2	This work
	Argentation	(K) 1.0	10°C , $(\text{CH}_2\text{OH})_2$	18
	Hydration ^{b)}	1.1×10^2	25°C , HClO_4 , H_2O	19
	Alcoholation	6.2×10^2	60°C (extrapolated), H_2SO_4 , methanol	20
	"	9.1×10^2	60°C (extrapolated), H_2SO_4 , ethanol	20
Styrene	Bromination	12.6	0°C , CCl_4	17
	"	4.8	0°C , CH_2Cl_2	17
	Polymerization	4.0	-78°C , $\text{SnCl}_4 \cdot \text{TCA}$, CH_2Cl_2	This work

Argentation	(K_1)0.41 (K_2)0.92	0°C, H ₂ O	21
π -complexation with I ₂	($\sum_i K_i$)0.53	room temp, isooctane	22

- a) The ratio of rate or equilibrium constant (k or K) of α -methyl-substituted reactants to that of α -unsubstituted ones.
- b) Reactant: p-methoxystyrene.

cationic polymerization and bromination occupies the intermediate state of protonation and complexation with silver ion or iodine.

This study shows that ethyl α -phenylvinyl ether (α -ethoxy- α -phenylethylene) does not produce a homopolymer under cationic mechanism. On the contrary, it is reported that ethyl β -phenylvinyl ether (α -ethoxy- β -phenylethylene) does homopolymerize cationically.²³ Therefore, it may be concluded that α,α -disubstituted ethylene suffers more steric hindrance than the α,β -disubstituted one does. On the other hand, many α,α -disubstituted ethylenes form homopolymers in radical polymerization, but the corresponding α,β -disubstituted ethylenes do not, with the exception of fluorine as a substituent. This leads one to suppose that the disposition of a propagating species and a monomer in the transition state of cationic polymerization differs from that of radical polymerization. The stage of complex formation between a carbocation and a double bond is concerned with the

rate-determining step in cationic polymerization, and it is probable that an α,α -disubstituted ethylene draws near to the active species with more difficulty than the corresponding α,β -disubstituted ethylene does. Accordingly, an α -substituent may hinder the reaction more than a β -substituent does in cationic polymerization. On the other hand, as a radical attacks β -carbon directly, so a β -substituent of a monomer hinders the approach of the active species more than an α -substituent does. For this reason, the case may become the reverse in radical polymerization.

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Chapter 6

Reactivity of 2-Alkoxybutadienes

Introduction

There have been a lot of investigations on the structure-reactivity relationship in cationic polymerization of alkyl vinyl ethers.^{1,2} The presence of oxygen adjacent to the vinyl group leads to a unique reactivity of alkyl vinyl ethers. Electrophilic addition reactions of linear conjugated dienes have also been investigated; the cationic polymerizations of butadiene³ and 2,4-hexadienes,⁴ and the structure,⁵ electrophilic reactions,⁶ and cationic polymerizations⁷ of 1-phenyl- and 1-alkoxybutadienes.

2-Alkoxybutadiene is regarded as an alkyl vinyl ether as well as a butadiene derivative. For the former case the α -vinyl group is a substituent, and for the latter case the 2-alkoxy group is a substituent. The importance of each substituent is dependent on the nature of the reaction. Studies on the effect of substituent in such a compound may, therefore, shed light on the nature of a reaction. For instance, Fedor has investigated whether 4-methoxy-3-buten-2-one and several 3-alkyloxycrotonates are hydrolyzed as a vinyl ether or as a vinyl ketone.⁸

The lone-pair electrons of oxygen in a vinyl ether migrate to the double bond and makes a vinyl ether peculiarly reactive in electrophilic reactions. It is interesting to know how this effect is manifested in a reaction of 2-alkoxybutadiene.

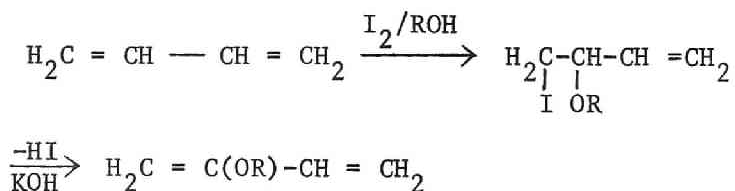
Another point of interest is that the coplanarity between diene and alkoxy groups, hence the reactivity, is affected by increasing bulkiness of alkyl group. It is not known how reactive a 2-alkoxybutadiene is in cationic polymerization and whether it produces a high polymer.

In this chapter, the molecular structure, properties, and cationic polymerizability of several 2-alkoxybutadienes are studied. The results are discussed in comparison with those of alkyl vinyl ethers.

Experimental

Materials

Five 2-alkoxybutadienes, that is, 2-methoxybutadiene (MOBD), 2-ethoxybutadiene (EOBD), 2-isopropoxybutadiene (IPOBD), 2-(tert-butoxy)butadiene (tBOBD), and 2-(2-chloroethoxy)butadiene (CEOBD), were prepared by the Petrow's method⁹ in the following process:



Boiling points and refractive indices of the 2-alkoxybutadienes prepared are given in Table I.

Tungsten hexachloride (extra pure) and iodine (E. Merck, resublimed reagent) were used without further purification. Titanium tetrachloride was purified by the distillation of commercial material (bp 136°C). Other catalysts and solvents

Table I. Boiling points, refractive indices, and uv spectrum data for 2-alkoxybutadienes

	bp, °C (lit)	n_D^{20} (lit, n_D^{15})	λ_{max} , nm ^{a)}
MOBD	75.0 (74.0-75.5)	1.4453 (1.4480)	233
EOBD	94.5 (92.5-93.5)	1.4417 (1.4430)	234
IPOBD	106 (105 -107)	1.4400 (1.4410)	237
tBOBD	125	1.4379	234
CEOBD	74 (30 mm)	1.4534	233

a) concn, 0.0500 mmol/l.

were purified as described in the previous chapters.

Procedures

Uv spectra of the alkoxybutadienes were measured in n-hexane (reagent for spectroscopy) on a Shimadzu MPS 50 spectrophotometer. Ir spectra of a neat sample were obtained by a Shimadzu IR27G grating spectrophotometer.

¹H nmr spectra were measured in 10 V/V % solution in carbon tetrachloride on a Varian HA-100 spectrometer. ¹³C nmr spectra were measured at 25.14 MHz on a JEOL PFT-100 spectrometer. The spectrum of a neat liquid was taken with accumulation of 100 scans by the Fourier transform method.

Polymerization procedure is similar to that described in a previous chapter.¹⁰

Method of Calculation

MINDO/2 formalism devised by Dewar¹¹ was used for the theoretical method and parametrizations without further modification. The convergence was judged from the energy level criterion of 1.0×10^{-3} eV in all the orbital energies. The atomic coordinates used for the 2-alkoxybutadienes and alkyl vinyl ethers are as follows: $\text{C}=\text{C}$ 1.34, $\text{C}=\text{O}$ 1.40, $\text{C}-\text{O}$ 1.43, $\text{C}-\text{C}$ 1.48, $\text{C}-\text{H}$ 1.08, $\text{C}-\text{H}$ 1.09; $\angle \text{C}-\text{O}-\text{C}$ 110° , $\angle \text{C}-\text{C}-\text{C}$ $\angle \text{C}-\text{C}-\text{O}$ $\angle \text{C}-\text{C}-\text{H}$ 109.5° , $\angle \text{C}=\text{C}-\text{C}$ $\angle \text{C}=\text{C}-\text{O}$ $\angle \text{C}=\text{C}-\text{H}$ 120° . The s-trans conformation of $\text{C}=\text{O}$ bond in alkyl vinyl ether, and the s-cis of $\text{C}=\text{O}$ bond and s-trans of $\text{C}=\text{C}$ bond in 2-alkoxybutadienes were assumed. Computations were made on a FACOM 230-60 computer at the Data Processing Center of Kyoto University.

Results and Discussion

The Molecular Structure and Properties of 2-Alkoxybutadienes

2-Alkoxybutadienes show a broad absorption in the uv region whose maximum is located in the range of 233-237 nm (see Table I). It is evident in Table I that the absorption shows a small red shift with increasing bulkiness of the alkyl group from methyl to isopropyl. The same trend has been found for alkyl vinyl ethers.^{12,13} tBOBD, however, shows an unexpected blue shift, which is quite different from tert-butyl vinyl ether. This could be explained in terms of the displanarity between the conjugated double bond and O-alkyl bond owing to steric hindrance.

Ir spectra of 2-alkoxybutadienes are shown in Figure 1. Absorptions due to symmetrical stretching vibration of the

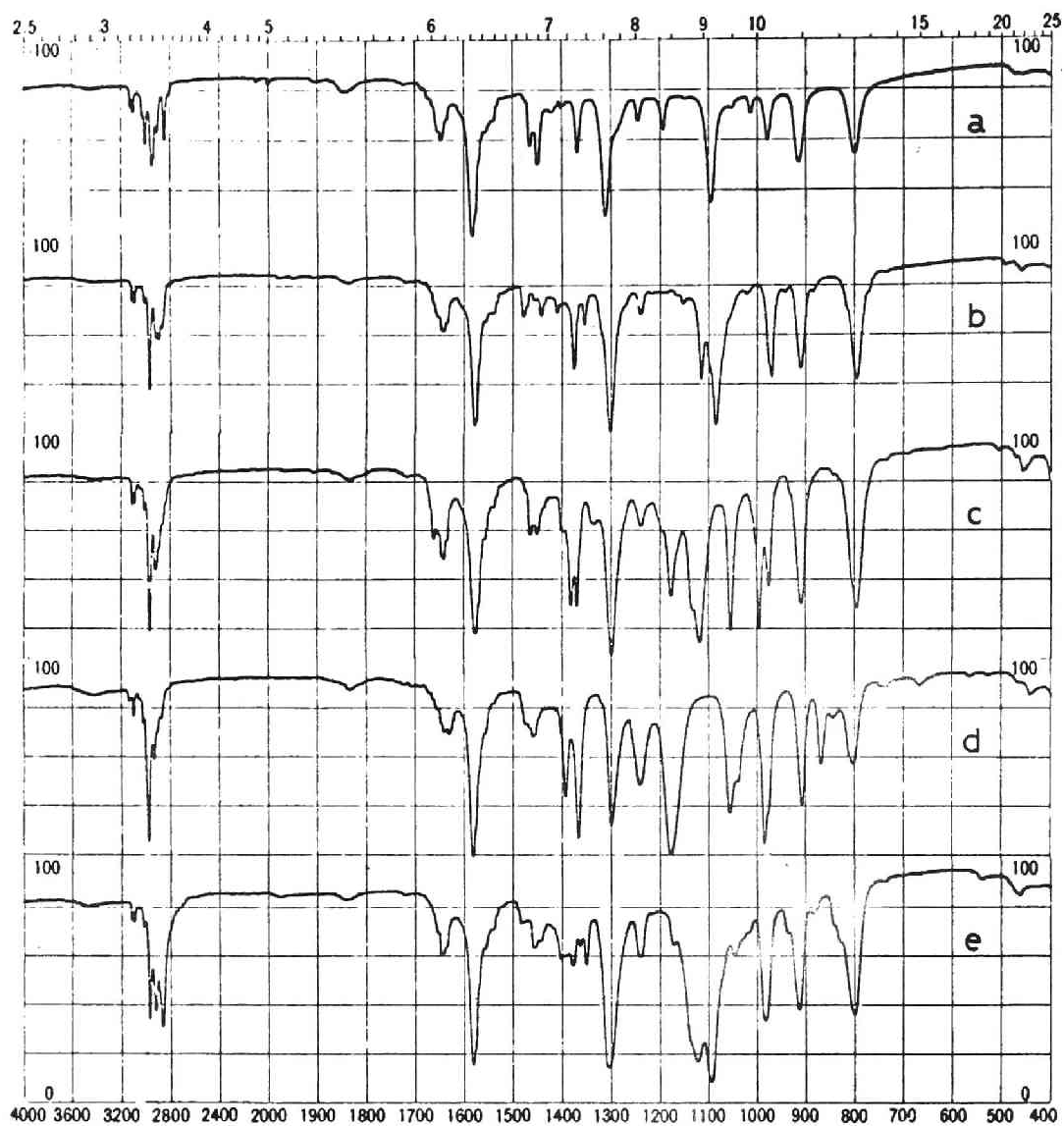
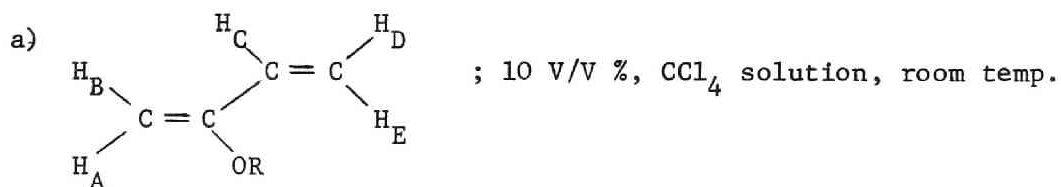


Figure 1. Ir spectra of 2-alkoxybutadienes. a, MOBD; b, EOBD; c, IPOBD; d, tBOBD; e, CEOBD.

Table II. ^1H chemical shifts and spin coupling constants of 2-alkoxybutadienes^{a)}

	Chemical shift, ppm					Coupling constant, cps		
	τ_A	τ_B	τ_C	τ_D	τ_E	J_{CD}	J_{CE}	J_{DE}
MOBD	5.94	5.97	3.95	4.99	4.52	10.6	17.1	-2.1
EOBD	5.97	5.99	3.95	4.99	4.50	10.5	17.4	-2.2
IPOBD	5.96	5.97	3.98	5.03	4.53	10.5	17.2	-2.3
tBOBD	5.71	5.72	3.97	5.06	4.60	10.3	17.0	-2.3
CEOBD	5.93	5.95	3.93	4.98	4.49	10.5	17.1	-2.2



ether linkage are observed at 1097 cm^{-1} in MOBD, and at 1120 and 1090 cm^{-1} in EOBD, while they are split and shifted in a complex manner in IPOBD and tBOBD. Asymmetrical stretching vibration of the ether linkage in a bulkier alkyl group shows a lower-frequency shift (MOBD 1312 cm^{-1} , tBOBD 1305 cm^{-1}).

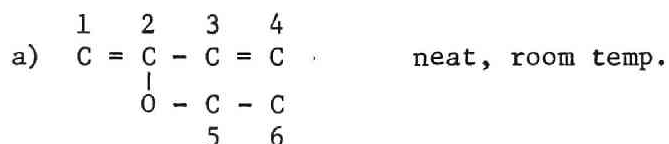
Chemical shifts and coupling constants in the ^1H nmr spectra of 2-alkoxybutadienes are given in Table II. J_{AB} could not be determined, as the chemical shifts of H_A and H_B are very close. It is noteworthy that τ_A and τ_B of tBOBD are exceptionally small as compared with other 2-alkoxybutadienes. This could also be accounted for by the destruction of the coplanarity between diene and O-alkyl bonds by steric hindrance.

The ^{13}C chemical shifts of 2-alkoxybutadienes are listed in Table III. Carbon 1 in 2-alkoxybutadienes is highly shielded and the value is very close to that of β -carbon in a corresponding alkyl vinyl ether.^{14,15} However, the chemical shift of carbon 1 in tBOBD indicates a distinct deshielding in comparison with other 2-alkoxybutadienes. This is also explained in terms of lesser conjugation of the lone-pair electrons in oxygen. The resonance peak of carbon 2 appears in low-field region. This is the case also for tBOBD, which implies the predominance of the inductive effect over the resonance effect for the shift of carbon 2. The chemical shifts of carbons 3 and 4 are comparatively insensitive to the kind of alkyl group.

The results of molecular-orbital calculation are shown in Table IV. The calculated ionization potentials of 2-alkoxybutadienes are smaller than those of alkyl vinyl ethers. The bulkier the alkyl group, the smaller the ionization potential in both classes of compounds. Total electron density on carbon 1 is large in a 2-alkoxybutadiene and that on carbon

Table III. ^{13}C chemical shifts of 2-alkoxybutadienes^{a)}

	Chemical shift ^{b)}					
	1	2	3	4	5	6
MOBD	86.18	159.61	133.55	113.99	54.34	
EOBD	86.61	158.79	133.89	113.79	62.78	14.44
IPOBD	87.44	157.09	134.57	113.79	68.61	21.67
tBOBD	95.69	155.83	136.61	114.04	77.00	28.56
CEOBD	87.05	158.59	133.60	114.13		



b) In ppm downfield from tetramethylsilane (192.8 ppm upfield from carbon disulfide).

2 is small. The same trend has been found with alkyl vinyl ethers, but the difference between carbon 1 and carbon 2 is more marked with 2-alkoxybutadienes. The total electron densities on carbons 1, 2, 3 and 4 tend to be alternating. Contrary to the total electron density, the electron density in π -orbital on carbon 1 decreases as the alkyl group becomes bulkier.

Table IV. Highest occupied energy level and electron densities of alkyl vinyl ethers and 2-alkoxybutadienes

	Highest occupied level, eV	Total electron density					π -Orbital electron density				
		C ₁ ^{b)}	C ₂	C ₃	C ₄	O	C ₁	C ₂	C ₃	C ₄	O
MVE ^{a)}	-9.4744	4.1250	3.6490			6.5173	1.1159	0.9424			1.9338
EVE	-9.4336	4.1271	3.6462			6.5271	1.1179	0.9407			1.9335
IPVE	-9.3092	4.1285	3.6525			6.5264	1.1193	0.9416			1.9187
tBVE	-9.3034	4.1284	3.6585			6.5354	1.1219	0.9390			1.9198
MOBD	-9.0104	4.2073	3.6259	4.0495	3.9810	6.5299	1.1679	0.9038	1.0345	0.9587	1.9261
EOBD	-8.9866	4.2082	3.6239	4.0497	3.9815	6.5388	1.1681	0.9034	1.0338	0.9597	1.9261
IPOBD	-8.7327	4.2323	3.6198	4.0503	3.9815	6.5476	1.1577	0.9025	1.0344	0.9596	1.9194
tBOBD	-8.4450	4.2717	3.6061	4.0522	3.9776	6.5843	1.1545	0.8898	1.0389	0.9541	1.9175

a) MVE: methyl vinyl ether, EVE: ethyl vinyl ether, IPVE: isopropyl vinyl ether, tBVE: tert-butyl vinyl ether.

b) Carbons are numbered as follows: $\begin{array}{c} 1 & 2 \\ \text{C} = & \text{C} \\ & | \\ & \text{OR} \end{array}$, $\begin{array}{c} 1 & 2 & 3 & 4 \\ \text{C} = & \text{C} - & \text{C} = & \text{C} \\ & | & & \\ & \text{OR} & & \end{array}$.

Table V. Cationic homopolymerization of EOBD^{a)}

Catalyst	Solvent	Temp, °C	Conversion, %	
			Monomer consumption	MeOH-insol. polymer
WCl ₆ ·TCA	Toluene	-78	7.2	~3
AcClO ₄	"	"	12.9	
Iodine	"	"	4.8	~3
TiCl ₄ ·TCA	"	"	8.7	
WCl ₆ ·TCA	"	0	46.8	5.6
AcClO ₄	"	"	55.3	
WCl ₆ ·TCA	n-Hexane	"	33.0	
"	CH ₂ Cl ₂	"	82.3	0
"	Nitroethane	"	~100	0
"	CCl ₄	"	54.4	

a) [M]₀ 1.0 mol/l; [C]₀ 5.0 mmol/l (-78°C),
2.5 mmol/l (0°C); polymn time 2 hrs.

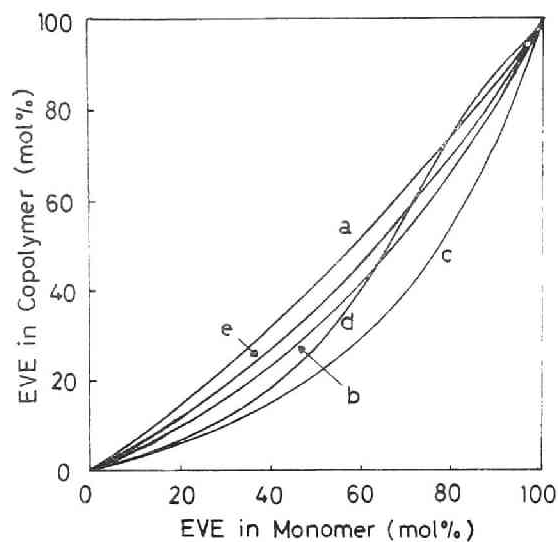


Figure 2. Copolymerization of ethyl vinyl ether (M_1) with 2-alkoxybutadienes (M_2) (-78°C , $[M]_0$ 1.0 mol/l, BF_3OEt_2 , toluene). M_2 : 1, MOBD; 2, EOBD; 3, IPOBD; 4, tBOBD; 5, CEOBD.

Table VI. Monomer reactivity ratios for the copolymerization of ethyl vinyl ether (M_1) with 2-alkoxybutadienes (M_2)^{a)}

M_2	r_1	r_2	$r_1 \times r_2$	$1/r_1$
MOBD	0.79 ± 0.06	1.28 ± 0.10	1.0	1.27
EOBD	0.49 ± 0.07	1.92 ± 0.17	0.94	2.04
IPOBD	0.28 ± 0.04	3.38 ± 0.40	0.93	3.57
tBOBD	1.24 ± 0.11	4.70 ± 0.38	5.82	0.81
CEOBD	0.65 ± 0.11	1.96 ± 0.26	1.23	1.54

a) $[M]_0$ 1.0 mol/l, BF_3OEt_2 , toluene, -78°C .

Reactivity of 2-Alkoxybutadienes in Cationic Polymerization

The cationic homopolymerization of EOBD was carried out using various catalysts and solvents (see Table V). The consumption of monomer was fairly rapid under the conditions described in Table V. However, only a small amount of methanol-insoluble polymer was produced. High-boiling components which are acceptable for dimers were not detected in the polymerization system through gas chromatography, so that most of the product is considered to be a methanol-soluble oligomer. The homopolymerization rate was similar to or a little smaller than ethyl vinyl ether.

Copolymerizations of 2-alkoxybutadienes with ethyl vinyl ether were attempted in order to know the relative reactivities of 2-alkoxybutadienes. The copolymerizations were performed in toluene by boron trifluoride diethyl etherate (BF_3OEt_2) at -78°C , total monomer concentration being 1.0 mol/l. The copolymer composition curves and monomer reactivity ratios are given in Figure 2 and Table VI, respectively. The products of r_1 and r_2 in the copolymerizations are approximately unity except for tBOBD. Reciprocal of r_1 increases in the order of MOBD < CEOBD < EOBD < IPOBD. This change with the kind of alkyl group is in the same direction as that of alkyl vinyl ethers but the effect of alkyl group is smaller in 2-alkoxybutadienes.^{2,16} With tBOBD, $1/r_1$ is peculiarly smaller and $r_1 \times r_2$ is much larger than unity. The result that only tBOBD gives a sigmoidal composition curve may be in close connection with the peculiar properties of tBOBD as shown in Tables I, II and III. For, a sigmoidal copolymer composition curve has often been found in the ionic copolymerization of monomers

which have a different kind of conjugation.^{10,17} As 2-alkoxybutadienes except for tBOBD assume a coplanar structure between diene and O-alkyl bonds, they behave similarly to alkyl vinyl ethers. However, the vinyl-ether-like character of tBOBD is weakened, and in consequence tBOBD might not copolymerize randomly with ethyl vinyl ether.

The investigations on the structure of oligomer of 2-alkoxybutadienes would help ascertain the polymerization mechanism, though it was not done in this experiment. Further, the structure of bromination product of 2-alkoxybutadienes is also interesting, since the polar bromination of an olefin proceeds under a comparatively similar mechanism to that of cationic polymerization.¹⁸

Following conclusions are drawn from the present investigation: 2-alkoxybutadienes have the molecular structure and properties similar to alkyl vinyl ethers, and highly reactive in cationic polymerization. tBOBD, however, behaves differently from other 2-alkoxybutadienes in cationic polymerization since the coplanarity between diene and O-alkyl bond cannot be maintained owing to steric hindrance.

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Chapter 7

Comparison of Polar Bromination with Cationic Polymerization

Introduction

Electrophilic addition reaction to an olefin involves acid-catalyzed hydration, the addition reactions of hydrogen halides and halogens, cationic polymerization, and so forth. Electrophilic complexation with olefins comprises complex formations of iodine or silver ion. It has been noticed that substituent effect is very much dependent on the nature of these reactions. For instance, α -methyl-substituted vinyl ethers or styrenes are 10^2 - 10^4 times as reactive in protonation and 0.4-1.0 times as reactive in argentation as the corresponding unsubstituted ones.¹ Further, β -methyl-substituted vinyl ethers are more reactive in cationic polymerization but less reactive in hydrolysis or argentation than the corresponding unsubstituted ones.² These results seem to offer a clue to elucidate the transition state in reactions of an olefin with an electrophile.

The hydrolysis of an alkyl vinyl ether³ and the hydration of styrene⁴ have been studied with keen interest of many physical organic chemists, and it has been established that the rate-determining step is the irreversible proton attack to β -carbon of the double bond. Yates has investigated the substituent effect in the polar bromination of styrenes in detail.^{5,6} It was concluded on the basis of the large ρ value observed that the substantial charge is localized on the α -carbon at the

transition state. With regard to an alkyl vinyl ether, there have been few studies on polar bromination.⁷ In general, it can be said that the feature of substituent effect in polar bromination in an aprotic solvent is not clear enough yet.

In this chapter, substituent effect in bromination is investigated making use of alkyl vinyl ethers and styrenes as reactant. The results are compared with corresponding data in cationic polymerization.

Experimental

Materials

tert-Butyl and isopropyl vinyl ethers (tBVE, IPVE) were synthesized by vinyl trans-etherification between ethyl vinyl ether and the pertinent alcohols.⁸ Methyl vinyl ether (MVE; Mitsubishi Kasei Co.) was used after drying by potassium hydroxide. The syntheses and purifications of other vinyl ethers (ethyl vinyl ether (EVE), ethyl propenyl ether (EPE), ethyl isopropenyl ether (EIPE), and 2-chloroethyl vinyl ether (CEVE)) and styrenes (styrene, α -methylstyrene (α MS), β -methylstyrene (β MS), p-methoxystyrene (pMOS), p-methylstyrene (pMS) and p-chlorostyrene (pCS)) were described in the previous chapters.^{9,10}

Solvents (carbon tetrachloride, methylene chloride, and acetic acid) were purified in the usual manners.

Procedure

Relative reaction rate of two vinyl compounds was determined by a competitive reaction at 0°C in carbon tetrachloride and

methylene chloride or at 25°C in acetic acid. A bromine solution was added dropwise to the reactant solution under vigorous stirring. On addition of the bromine solution, the color of bromine faded almost instantaneously in methylene chloride and acetic acid solution, but remained for some time in carbon tetrachloride solution. At given intervals of bromine addition, the aliquot sample was taken out of the solution with a microsyringe and the concentrations of reactants were determined by gas chromatography. The relative reactivity was determined by next equation assuming the first-order dependence on the concentration of vinyl compounds:

$$k_2/k_1 = \ln ([R_2]/[R_2]_0) / \ln ([R_1]/[R_1]_0)$$

where $[R_1]$, $[R_2]$ and $[R_1]_0$, $[R_2]_0$ mean the concentrations of two kinds of reactants after and before the reaction, respectively.

Results

Dependence of Relative Reactivity on Bromine Concentration

A stoichiometric amount of bromine was consumed by the olefinic double bond. The absence of the isomerization of cis- and trans- β -methyl compounds during the reaction was confirmed by gas chromatography. The present reaction is considered to be electrophilic since hydroquinone and oxygen did not affect the relative reactivity.

The influence of bromine concentration in the styrene- α MS system is shown in Table I. Here, "bromine concentration" refers to the concentration of the added bromine solution.

Table I. Effect of reaction conditions on k_2/k_1 value
in the styrene (R_1)- α MS(R_2) system at 0°C

Solvent	$[R]_0$, mol/l	$[Br_2]$, mol/l ^{a)}	k_2/k_1
CH ₂ Cl ₂	0.50	0.50	1.48
	0.20	"	1.50
	0.50	0.30	1.87
	"	0.125	2.71
	"	0.063	4.70
	0.20	0.025	4.82
	"	"	4.55 ^{b)}
CCl ₄	0.50	0.50	6.10
	"	0.30	6.15
	"	0.125	8.83
	"	0.063	12.7
	0.20	0.025	12.6

a) $[Br_2]$: the concn of bromine solution added.

b) Hydroquinone is added.

The bromine concentration in the reaction mixture must be more dilute, since the slow addition and the vigorous stirring enables a homogeneous mixing. The relative reactivity of α MS increases with the decrease in bromine concentration both in carbon tetrachloride and methylene chloride. It was, however, unaffected when the bromine concentration is lower than 0.060 mol/l. Thus, further experiments were performed at 0.025 mol/l

of bromine concentration.

The Reactivity of Various Styrene Derivatives and Alkyl Vinyl Ethers

The relative reactivities of several styrene derivatives in reference to styrene, k_2/k_1 are shown in Table II. As is seen from Table II, α MS is 4-13 times as reactive as styrene. *cis*- β MS is less reactive, but *trans*- β MS is more reactive than styrene. The relative reactivity of α MS does not change in methylene chloride and acetic acid but increases in carbon tetrachloride. The relative reactivities of three ring-substituted styrenes were also determined. They were correlated better with Hammett's σ value than with Brown's σ^+ value. The ρ values were -4.06, -1.99 and -3.22 in carbon tetrachloride, methylene chloride and acetic acid, respectively.

The k_2/k_1 values of vinyl ethers are listed in Table III. Here, EVE is used as the reference compound. α -Methyl substitution enhances the reactivity by ca. three times. *cis*- and *trans*- β -methyl substitution reduces the reactivity slightly. As to the change in the alkoxy group, for instance, tBVE is 4-5 times more reactive than EVE. The relative reactivities of alkyl vinyl ethers were correlated well with Tafts' σ^* value. ρ values were -2.9 and -3.6 in carbon tetrachloride and methylene chloride, respectively. Solvent effect was small although only two solvents were tested.

A large solvent effect has been observed in the cationic copolymerization of CEVE with styrene derivatives, as described in a previous chapter.¹¹ In order to know whether a similar effect is found in polar bromination, solvent effect on k_2/k_1

Table II. k_2/k_1 value of styrene derivatives
(R_1 : styrene)^{a)}

R_2	CCl_4	CH_2Cl_2	CH_3CO_2H
α MS	12.6	4.82	4.53
cis- β MS	0.70	0.74	0.42
trans- β MS	1.35	1.44	1.18
pMS	21.6	3.04	9.11
pMS	5.12	2.74	4.64
pCS	0.18	0.35	0.24
ρ	-4.06	-1.99	-3.22
r	0.991	0.989	0.997

a) $[Br_2]$, 0.025 mol/l; $[R]_0$, 0.20 mol/l,
0°C (CCl_4 , CH_2Cl_2), 25°C (CH_3CO_2H).

values of pMS, pMS and α MS (R_2) in reference to CEVE (R_1) was examined (see Table IV). Clearly, the reactivities of the styrene derivatives relative to CEVE become greater in polar methylene chloride than in nonpolar carbon tetrachloride. The change with solvent is the greatest for pMS as a styrene derivative which has the poorest reactivity in the three styrenes.

Table III. k_2/k_1 value of vinyl ethers
(R_1 : EVE)^{a)}

R_2	CCl_4	CH_2Cl_2
EIPE	2.96	3.19
cis-EPE	0.73	0.94
trans-EPE	—	0.69
tbVE	3.89	4.97
IPVE	2.09	2.51
MVE	0.53	0.42
CEVE	0.36	0.54
ρ	-2.9	-3.6
r	0.997	0.994

a) $[Br_2]$, 0.025 mol/l; $[R]_0$, 0.20 mol/l; 0°C.

Table IV. k_2/k_1 value of CEVE (R_1) and
substituted styrenes (R_2)^{a)}

R_2	CCl_4	CH_2Cl_2
pMOS	0.68	0.99
pMS	~0	0.20
α MS	0.08	0.40

a) $[Br_2]$, 0.025 mol/l; $[R]_0$, 0.20 mol/l; 0°C.

Discussion

The bromination was performed with 0.20 mol/l of total olefin and 0.025 mol/l of bromine. This condition was chosen because the change of the reagent concentration in this range did not affect k_2/k_1 , and cationic polymerization is often carried out in this concentration range. Carbon tetrachloride and methylene chloride are aprotic and often used in cationic polymerization. The real bromine concentration in the reaction seems to be considerably smaller than 0.025 mol/l. The substituent effect observed in this investigation is, however, not so large as that reported by Yates.^{5,6} Therefore, it is probable that the reaction is second-order with respect to the bromine concentration under the present condition.

α -Methyl substitution enhances the reactivity of styrene by ca. 5-12 times and that of EVE by ca. three times. The corresponding values in cationic polymerization are 4.0 and 7.7 with styrene and EVE, respectively. The β -methyl substitution induces rather small changes of reactivity in polar bromination as well as in cationic polymerization.¹⁰ From these results, it can be said that the relative reactivities of olefins in polar bromination are in good agreement with those in cationic polymerization but very different from those in protonation.¹

The relative reactivities of ring-substituted styrenes in polar bromination correspond well to those in cationic polymerization,¹² though the value of ρ_{MOS} is rather small. ρ for a series of alkyl vinyl ethers is ca. -3 — -3.5, which is less negative than ρ in hydrolysis (-4.5)¹³ and cationic polymerization (-4.3).¹⁴

The solvent effect observed on the relative reactivity of CEVE to styrene derivatives is similar to the solvent effect observed in cationic polymerization,¹¹ that is, a styrene derivative becomes more reactive in a more polar solvent. This is explained in terms of the selective solvation of an ionic species by a vinyl ether in a nonpolar solvent.

It is concluded from the results obtained in this study that the bromination of a vinyl ether and a styrene exhibits a substituent effect smaller than protonation and especially similar to cationic polymerization in electrophilic addition reactions. This is reminiscent that the positive charge may not localize on the α -carbon at the transition state under the conditions in this experiment in polar bromination.

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PART III

STRUCTURE AND REACTIVITY OF MONOMERS IN CATIONIC POLYMERIZATION

Chapter 8

Theoretical Consideration on the Reactivity of Vinyl Ethers and β -Substituted Vinyl Ethers

Introduction

In radical polymerization, α,β -disubstituted olefins are reluctant to polymerize because of the steric hindrance between the β -substituent in a growing polymer end and that in an incoming monomer, except in the case of cyclic compounds such as vinylene carbonate and maleimide. With a cationic catalyst, however, styrene and vinyl ether derivatives carrying the β -methyl group produced a high polymer. These results suggest that the spatial position of the β -methyl group in the transition state of the propagation step in cationic polymerization is different from that in radical polymerization.¹

In cationic polymerization, the introduction of a β -methyl group has been found to reduce the reactivity of styrene derivatives^{1,2} but to increase the reactivity of vinyl ethers.³⁻⁵ For the reason of the opposing effects of the β -methyl group on the reactivity of styrene and vinyl ether derivatives, two possibilities should be considered; (1) the effect of β -methyl group on the electron distribution in monomer depends on the kind of monomer; (2) the conformation of transition state in the propagation reaction changes with the kind of monomer.

In this chapter, to elucidate the rate-determining step in the propagation reaction, the electron distribution of vinyl ether derivatives, unsaturated hydrocarbons and related carbocations was calculated by the extended Hückel method,⁶ because the

simple Hückel method leaves some ambiguities in the parametrization for alkyl groups and in the study on the reactivity of geometric isomers. The validity of the calculated value of the π -electron distribution has been confirmed by the chemical shifts in the ^{13}C nmr spectrum of the β -carbon.⁷ By using the value of the electron distribution in a monomer, several reactivity indices were calculated by the same treatment as in the simple Hückel method. A possible reaction mechanism is proposed on the basis of comparisons of the reactivity indices with the experimental results.

Calculation of Electron Distribution

Method of Calculation

A molecular orbital is given as a linear combination of valence atomic orbitals on all atoms in a molecule.⁶ In this study, the following values were used for the Coulomb integrals; H_{1s} , -13.60 eV; C (2s), -21.43 eV; C (2p), -11.42 eV; O (2s), -35.30 eV; O (2p), -15.45 eV. The resonance integral H_{ij} was approximated by eq 1:

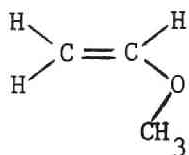
$$H_{ij} = 0.5 K (H_{ii} + H_{jj}) S_{ij} \quad (1)$$

with $K = 1.75$, where H_{ii} and H_{jj} are the Coulomb integrals, and S_{ij} is the overlap integral which was calculated by using Slater atomic orbitals.

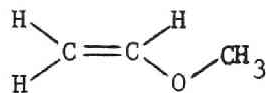
The geometric structure of vinyl ether derivatives was described by the bond distance and the bond angle as follows; saturated C-H, 1.09 Å; unsaturated C-H, 1.08 Å, C-C, 1.54 Å;

C=C, 1.35 Å, saturated C-O, 1.427 Å; unsaturated C-O, 1.42 Å; the tetrahedral angle $109^{\circ}28'$ for a saturated carbon, the trigonal angle 120° for an unsaturated carbon; and 107° for ether oxygen $\angle\text{COC}$. The bond distance and the bond angle used for unsaturated hydrocarbons were the same as those for vinyl ether derivatives except for unsaturated C-H; 1.07 Å, C=C, 1.34 Å; C-C in aromatics, 1.39 Å; and unsaturated C-C₆H₅ (aromatics), 1.47 Å. For calculations on a carbocation, the bond distance between C⁺ and an adjacent carbon atom was assumed to be 1.54 Å; other values were the same as those for the corresponding monomer molecule. Although the calculation was based on approximate values of bond distance and bond angle, the relative electron distribution and the relative reactivity indices may deserve discussion.

The electron distribution in vinyl ethers and their derivatives was computed for the conformation in which a hydrogen atom of a methyl group eclipses the olefinic double bond as well as the unsaturated hydrocarbons. Problems arise with the conformation of the methyl vinyl ether. The presence of rotational isomers around the C-O bond was observed by the infrared spectrum of methyl vinyl ether. Owen, et al.,⁹ reported that methyl vinyl ether existed predominantly in the s-cis form (I) in gas phase, and the s-trans form (II) was stabilized in polar solvents at room temperature. Also, Mikawa, et al.,¹⁰ confirmed the existence of rotational isomers in cis-β-chlorovinyl methyl ether.



I



II

Although the s-cis form has been found to predominate in methyl vinyl ether, the s-cis form seems unstable because of steric interaction between an alkoxy group and a β -hydrogen, in particular, when an alkyl group becomes bulkier and branched. Therefore, to simplify the calculation, only the s-trans form was considered in this paper for all vinyl ether derivatives, including methyl vinyl ether.

For the computation of the electron distribution in unsaturated hydrocarbons, the conformation in which the hydrogen atom of a methyl group eclipses the olefinic double bond was assumed according to Hoffmann's result.⁶

Results of calculations

Table I shows the atomic population (M_x) on the olefinic carbons and the ether oxygen. M_x is defined by eq 2 and corresponds to the total electron density,

$$M_x = \sum_r^x N_r \quad (2)$$

where N_r is the atomic orbital population given by eq 3, and C_r^j and C_s^j are the coefficients of the r-th and s-th atomic orbitals in the j-th molecular orbitals.

$$N = 2 \sum_j^{\text{occ}} \sum_s C_r^j C_s^j S_{rs} \quad (3)$$

When M_x is larger than 1, 4, and 6 for hydrogen, carbon, and oxygen atoms, respectively, the atom is more electron-rich than the neutral atom.

Table I. Atomic population and atomic orbital population of vinyl ethers and β -substituted vinyl ethers

Monomer	Atomic population			Atomic orbital population of π -orbital			Atomic orbital population of highest occupied level in π -orbital		
	C _{β}	C _{α}	O	C _{β}	C _{α}	O	C _{β}	C _{α}	O
β α									
CH ₂ =CHOCH ₃	4.3838	3.5410	6.9690	1.1312	0.9200	1.9438	0.5331	0.3385	0.1150
cis-CH ₃ CH=CHOCH ₃	4.1546	3.6688	6.9718	1.0426	1.0389	1.9493	0.4060	0.4033	0.0851
trans-CH ₃ CH=CHOCH ₃	4.1548	3.6674	6.9745	1.0409	1.0370	1.9515	0.4005	0.3970	0.0911
cis-C ₂ H ₅ CH=CHOCH ₃	4.1739	3.6672	6.9718	1.0437	1.0384	1.9492	0.3667	0.3860	0.0762
trans-C ₂ H ₅ CH=CHOCH ₃	4.1738	3.6657	6.9747	1.0420	1.0363	1.9515	0.3609	0.3778	0.0829
cis-CH ₃ OCH=CHOCH ₃	3.6683	3.6683	6.9721	1.0422	1.0422	1.9525	0.3985	0.3985	0.0952
trans-CH ₃ OCH=CHOCH ₃	3.6714	3.6714	6.9665	1.0419	1.0419	1.9527	0.3975	0.3975	0.0961
CH ₂ =CHOC ₂ H ₅	4.3841	3.5394	6.9776	1.1316	0.9197	1.9438	0.5160	0.3255	0.1262

Table II. Atomic population and atomic orbital population of unsaturated hydrocarbons

Monomer	Atomic population		Atomic orbital population of π -orbital		Atomic orbital population of highest occupied level in π -orbital	
	C_β	C_α	C_β	C_α	C_β	C_α
$\beta \quad \alpha$ $\text{CH}_2=\text{CHCH}_3$	4.3807	4.0210	1.1277	0.9197	0.5389	0.3451
cis- $\text{CH}_3\text{CH}=\text{CHCH}_3$	4.1533	4.1533	1.0433	1.0433	0.4209	0.4209
trans- $\text{CH}_3\text{CH}=\text{CHCH}_3$	4.1489	4.1489	1.0390	1.0390	0.4017	0.4017
$\text{CH}_2=\text{C}(\text{CH}_3)_2$	4.4880	3.8263	1.2264	0.8563	0.5880	0.2839
$\text{CH}_2=\text{CHC}_6\text{H}_5$	4.3255	4.0751	1.0545	0.9598	0.2878	0.0983
trans- $\text{CH}_3\text{CH}=\text{CHC}_6\text{H}_5$	4.0804	4.1958	0.9509	1.0692	0.2656	0.1917

For the styrene and propylene derivatives, M_x values on the olefinic carbons are shown in Table II. In the unsaturated hydrocarbons as well as the vinyl ether derivatives, M_x on the β -carbon decreased and M_x on the α -carbon increased with introducing an electron-donating group on the β -carbon.

It is very difficult to confirm the reliability of values shown in Tables I and II, because we have no direct method to measure the electron density. However, it is reported⁷ that the values of the atomic orbital population in the π -orbital are closely correlated with the chemical shift of the ^{13}C nmr spectrum of the olefinic β -carbon. Since the nmr spectrum undergoes an upfield shift with increasing π -electron density,^{11,12} the calculations for the vinyl ether derivatives prove to be reasonable for the prediction of the electron distribution. Also, in the aliphatic unsaturated hydrocarbons, a downfield shift of the ^{13}C nmr spectrum of the olefinic β -carbon and an upfield shift of the olefinic α -carbon resulted on introduction of an alkyl group on the olefinic β -carbon.¹³ This fact also supported the validity of the calculated electron distribution for propylene derivatives.

Reactivity Indices

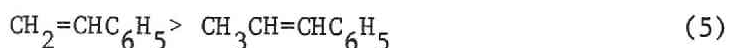
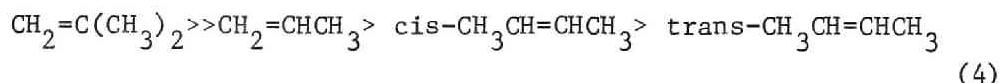
By using the calculated value of the electron distribution, reactivity indices for an electrophilic reaction were calculated by a procedure similar to the simple Hückel method.

Electrostatic Method

The carbocation will attack the atom with the largest electron density in the cationic polymerization where the

electrophilic addition reaction to a monomer takes place. Therefore, the reactivity of monomer may be estimated from the values of the atomic population (M_x) shown in Tables I and II. However, since the polymerization is caused by the interaction of an electrophilic reagent with the π -electron of a monomer, the monomer reactivity estimated from the atomic orbital population of the π -orbital should be more suitable for predicting the monomer reactivity than that from the atomic population. Tables I and II also show the values of the atomic orbital population of the π -orbital. As shown in Tables I and II the values of the atomic orbital population show the same tendency as the values of the atomic population.

In general, the relative reactivities of unsaturated hydrocarbons in the cationic polymerization or oligomerization tend to decrease in the following order:^{1,2,14}



Either the values of the atomic population or the values of atomic orbital population in π -orbital coincided with the order of the relative reactivities of monomers shown in (4) and (5). Although the values of the atomic population and the atomic orbital population on the β -carbon were in agreement with the order of reactivities of styrene and β -methylstyrene, the atomic population on the α -carbon of β -methylstyrene was larger than that of the β -carbon as shown in Table II, which predicts the α -carbon atom undergoes electrophilic attack. Experimentally, attack by

an electrophilic reagent on the β -carbon was observed.¹⁵ This discrepancy could be explained by the frontier electron density¹⁶ as described below.

On the other hand, in the vinyl ether derivatives, there was no correlation between the atomic population or the atomic orbital population and the relative reactivity of monomers.

Frontier Electron Method

The reactivity of an electrophilic reagent may be discussed more reasonably on the basis of the partial atomic orbital population of the highest occupied level in the molecular orbitals than on the basis of the atomic population or the atomic orbital population. As shown in the last column of Tables I and II, the value of the partial atomic orbital population in the highest occupied level is in agreement with the experimental results for the unsaturated hydrocarbons and shows that the carbocation will attack the β -carbon even in β -methylstyrene. Nevertheless, the relative reactivity of the vinyl ether derivatives is not satisfactorily explained by the value of the partial atomic orbital population of the highest occupied level.

Total Electron Energy

The total electron energy of a monomer or a carbocation is given by eq 6, where ϵ_i is the energy of the i -th molecular orbital. Table III shows the total electron energy of monomers and their related carbocation

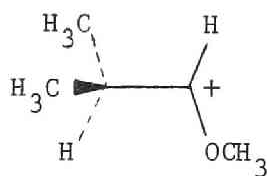
$$E = 2 \sum_{i}^{\text{occ}} \epsilon_i \quad (6)$$

Table III. Total electron energy

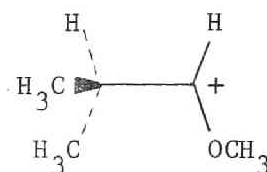
Monomer	Total electron energy, eV		
	Monomer	Carbocation	$E_{c^+} - E_M^a)$
$\text{CH}_2=\text{CHOCH}_3$	-450.380	-559.106	-108.726
cis- $\text{CH}_3\text{CH}=\text{CHOCH}_3$	-554.734	-662.965	-108.231
trans- $\text{CH}_3\text{CH}=\text{CHOCH}_3$	-554.745	-662.965	-108.220
cis- $\text{C}_2\text{H}_5\text{CH}=\text{CHOCH}_3$	-659.031	—	—
trans- $\text{C}_2\text{H}_5\text{CH}=\text{CHOCH}_3$	-659.041	—	—
cis- $\text{CH}_3\text{OCH}=\text{CHOCH}_3$	-689.726	—	—
trans- $\text{CH}_3\text{OCH}=\text{CHOCH}_3$	-689.669	—	—
$\text{CH}_2=\text{CHOC}_2\text{H}_5$	-554.926	-663.770	-108.845
$\text{CH}_2=\text{CHCH}_3$	-315.362	-424.222	-108.860
cis- $\text{CH}_3\text{CH}=\text{CHCH}_3$	-419.661	-528.244	-108.582
trans- $\text{CH}_3\text{CH}=\text{CHCH}_3$	-419.805	-528.244	-108.439
$\text{CH}_2=\text{C}(\text{CH}_3)_2$	-419.865	-528.979	-109.113
$\text{CH}_2=\text{CHC}_6\text{H}_5$	-703.028	—	—
trans- $\text{CH}_3\text{CH}=\text{CHC}_6\text{H}_5$	-807.479	—	—

a) Total electron energy of CH_3^+ group; planar type -110.001 eV; tetrahedral type, -108.984 eV.

assuming a structure with a methyl group on the β -carbon for simplicity. For example, structure III was proposed for a carbocation produced from methyl trans-propenyl ether. As the carbocation (IV) formed from cis-isomer should be very unstable, the structure of the carbocation (III) was assumed also for the methyl cis-propenyl ether carbocation.



III



IV

The difference between the total electron energy of a carbocation and that of monomer ($E_C^+ - E_M$) corresponds to the heat of a reaction, because the sum of E_M and the electron energy of the methyl carbocation corresponds to the total electron energy of the initial system, and E_C^+ to that of the reaction product, respectively. If the same reaction mechanism applies to each monomer, the value of ($E_C^+ - E_M$) may serve as an index of the activation energy. On introducing a methyl group onto the β -carbon of an olefinic double bond, the difference $E_C^+ - E_M$ is reduced by 0.4 eV to 0.5 eV, as shown in the last column of Table III. The results of calculation were in agreement with the experimental results for unsaturated hydrocarbons but not for the vinyl ether derivatives.

Superdelocalizability

The stabilization energy due to the hyperconjugation of

Table IV. Superdelocalizability (S_r^E) and delocalization energy for complex formation (ΔE) of vinyl ethers and β -substituted vinyl ethers

Monomer	$S_r^E \times 10^2, \text{eV}^{-1}$			$E \times 10^2, \gamma/\text{eV}$			
	C_β	C_α	0	$C_\beta + C_\alpha$	$C_\beta + 0$	$C_\alpha + 0$	$C_\alpha + C_\beta + 0$
$\text{CH}_2=\text{CHOCH}_3$	3.6089	2.6501	6.5115	12.2004	7.5585	9.2771	16.2655
cis- $\text{CH}_3\text{CH}=\text{CHOCH}_3$	3.2931	3.2575	6.5512	12.7360	7.2791	9.5797	16.4935
trans- $\text{CH}_3\text{CH}=\text{CHOCH}_3$	3.2934	3.2533	6.5801	12.7504	7.3139	9.5279	16.4655
cis- $\text{C}_2\text{H}_5\text{CH}=\text{CHOCH}_3$	3.2953	3.2599	6.5588	12.8001	7.2911	9.5833	16.4869
trans- $\text{C}_2\text{H}_5\text{CH}=\text{CHOCH}_3$	3.2952	3.2545	6.5797	12.7411	7.1774	9.5298	16.4595
cis- $\text{CH}_3\text{OCH}=\text{CHOCH}_3$	3.2310	3.2310	6.5272	12.5289	9.4186	9.4186	—
trans- $\text{CH}_3\text{OCH}=\text{CHOCH}_3$	3.2302	3.2302	6.5855	12.5303	9.5006	9.5006	16.2883
$\text{CH}_2=\text{CHOC}_2\text{H}_5$	3.6106	2.6484	6.5122	12.2010	7.5711	9.2670	16.3681

Table V. Superdelocalizability (S_r^E) and delocalization energy for complex formation (ΔE) of unsaturated hydrocarbons

Monomer	$S_r^E \times 10^2, \text{ eV}^{-1}$		$\Delta E \times 10^2, \gamma/\text{eV}$
	C_β	C_α	$C_\beta \times C_\alpha$
$\text{CH}_2=\text{CHCH}_3$	3.5913	2.6549	12.2261
cis- $\text{CH}_3\text{CH}=\text{CHCH}_3$	3.2806	3.2806	12.7335
trans- $\text{CH}_3\text{CH}=\text{CHCH}_3$	3.2601	3.2601	12.7135
$\text{CH}_2=\text{C}(\text{CH}_3)_2$	4.0873	2.3964	12.4095
$\text{CH}_2=\text{CHC}_6\text{H}_5$	3.3514	2.6986	11.6351
trans- $\text{CH}_3\text{CH}=\text{CHC}_6\text{H}_5$	2.9633	3.2556	11.9209

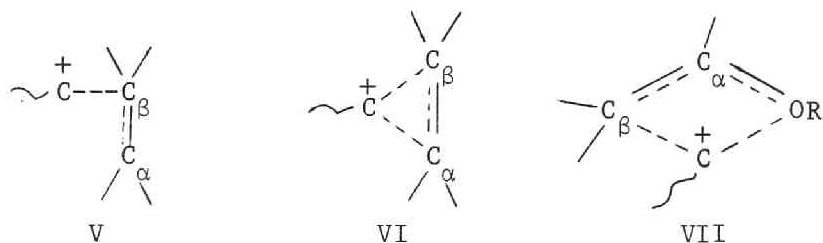
π -electrons in the transition state is approximately proportional to the superdelocalizability.¹⁷ Here, the superdelocalizability for the electrophilic reaction in the extended Hückel method, S_r^E , is tentatively given in eq 7, where C_r^j is the coefficient of the r -th $p\pi$ -atomic orbital in the j -th π -molecular orbital.

$$S_r^E = 2 \sum_j^{\text{occ}} (C_r^j)^2 / -\epsilon_j \quad (7)$$

The calculated values of S_r^E are summarized in Tables IV and V for vinyl ether derivatives and unsaturated hydrocarbons, respectively. According to the definition of eq 7, the position with a large S_r^E in a monomer is attacked by a carbocation, and a molecule consisting of atoms having a larger S_r^E value is more reactive than one having atoms with a small S_r^E value. As shown in Tables IV and V, S_r^E can explain the reactivity of the unsaturated hydrocarbons, but not the vinyl ether derivatives. This situation has been met with other reactivity indices.

Stabilization Energy due to Delocalization

S_r^E represents the delocalization energy acquired in the interaction of a carbocation with one atom in a monomer as shown in structure V. The alternatives, however, can be considered as a model for the interaction between a carbocation and a monomer, for example, the structure VI, in which carbocation forms a complex with two olefinic carbon atoms,⁴ or the structure VII, in which a carbocation interacts with the β -carbon and the ether oxygen.⁸



The π -electronic stabilization energy (ΔE) accompanying the delocalization (a complex formation) from the occupied orbital of the r-th, s-th atoms and so onto the vacant orbital of the carbocation is approximately given by eq 8,¹⁸ where γ is the resonance integral between the electron acceptor and donor and is assumed for simplicity to be constant for any type of interactions. More exactly, the denominator of eq 8 may be written as the difference between the energy level of the occupied orbital of the monomer and that of the vacant orbital of the carbocation. ΔE values calculated with eq 8 are summarized in Tables IV and

$$\Delta E = \sum_j^{\text{occ}} [2(C_r^j + C_s^j + \dots)^2 / -\epsilon_j] \gamma \quad (8)$$

V, where the atoms indicated on the second top row are those assumed to have interaction with carbocation. ΔE values shown in the $(C_\alpha + C_\beta)$ column do not explain the reactivity order of unsaturated hydrocarbons, whereas those in the $(C_\alpha + C_\beta + 0)$ column describe well the reactivity of vinyl ether derivatives. The latter will be discussed in more detail in the next section.

Discussion

With the unsaturated hydrocarbons, a satisfactory parallel

was found between the relative reactivity in the cationic polymerization and the various reactivity indices on the β -carbon of a monomer. However, $\Delta E(C_\alpha + C_\beta)$ did not explain the relative reactivity of monomers. These results suggest that the transition state for the rate-determining step in the propagation reaction is depicted by the structure V, in which the carbocation interacts with the β -carbon of the monomer, but not by the structure VI, in which carbocation forms a complex with the α - and β -carbons.

On the other hand, in the vinyl ether derivative, the introduction of an electron-donating group on the β -carbon did not decrease the reactivity of vinyl ethers except for a monomer with a bulky α - and/or β -substituent. Table VI shows the relative reactivity of vinyl ether derivatives obtained in the copolymerization catalyzed by BF_3OEt_2 at low temperatures.¹⁹ Considering the interaction of a carbocation only with the β -carbon in a monomer, the reactivity indices showed that the introduction of a β -substituent decreased the reactivity of the vinyl ether derivatives as well as of the unsaturated hydrocarbons. Therefore, the transition state in the propagation reaction of the vinyl ether derivatives could not be explained by the model V. Also, S_r^E values with respect to the α -carbon or the ether oxygen did not explain the relative reactivity of the vinyl ether derivatives as shown in Table VI.

Therefore, we should discuss structures by which the carbocation interacts with two or three atoms in a monomer to explain the relative reactivity of the vinyl ether derivatives. For structure VI, in which the carbocation reacts with the α - and β -carbons, $\Delta E(C_\alpha + C_\beta)$ could not explain the increase of the reactivity on introducing the β -methoxyl group and the reactivity

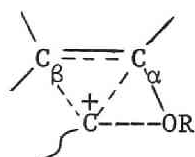
Table VI. Comparison between relative reactivity and superdelocalizability (S_r^E) or delocalization energy for complex formation (ΔE) of vinyl ether derivatives in cationic polymerization

		Methyl and ethyl vinyl ether (MVE and EVE)	MVE, methyl propenyl ether (MPE) and 1,2-dimethoxyethylene (DME)	MVE and methyl butenyl ether (MBE)
Experimental result ^{a)}		MVE<EVE	trans-DME<MVE<trans-MPE<cis-MPE<cis-DME	trans-MBE<MVE<cis-MBE
S_r^E	C_β	MVE<EVE	trans-DME \approx cis-DME<trans-MPE \approx cis-MPE<MVE	trans-MBE \approx cis-MBE<MVE
	C_α	EVE<MVE	MVE<trans-DME \approx cis-DME<trans-MPE<cis-MPE	MVE<trans-MBE<cis-MBE
	0	MVE \approx EVE	MVE<cis-DME<cis-MPE<trans-MPE<trans-DME	MVE<cis-MBE<trans-MBE
ΔE	$C_\beta + C_\alpha$	MVE \approx EVE	MVE<cis-DME<trans-DME<cis-MPE<trans-MPE	MVE<trans-MBE<cis-MBE
	$C_\beta + 0$	MVE<EVE	cis-MPE<trans-MPE<MVE<cis-DME<trans-DME	trans-MBE<cis-MBE<MVE
	$C_\alpha + 0$	EVE<MVE	MVE<cis-DME<trans-DME<trans-MPE<cis-MPE	MVE<trans-MBE<cis-MBE
	$C_\beta + C_\alpha + 0$	MVE<EVE	MVE<trans-DME<trans-MPE<cis-MPE<cis-DME	MVE<trans-MBE<cis-MBE

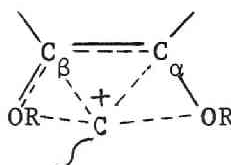
a) Catalyst, BF_3OEt_2 ; polymerization temp, -78°C .¹⁷

difference between methyl and ethyl vinyl ethers. In structure VII proposed by Ledwith, et al.,⁸ $\Delta E(C_\beta + O)$ does not increase on introduction of the β -methyl group. Moreover, as the sign of the coefficient of the highest occupied atomic orbital of olefinic carbons is different from that of ether oxygen, $\Delta E(C_\beta + O)$ is small and structure VII is not suitable as the model of the transition state. For the same reason, $\Delta E(C_\alpha + O)$ gave a small value. For this structure, the increase of the reactivity due to the introduction of a β -methoxyl group and the higher reactivity of ethyl vinyl ether compared to methyl vinyl ether could not be explained.

Structure VIII was proposed for the transition state to explain the relative reactivity of the vinyl ether derivatives.



VIII



IX

As *cis*-1,2-dimethoxyethylene has two ether oxygen atoms on the same side of the olefinic double bond, structure IX was assumed for the transition state. Further studies are necessary for a direct comparison of $\Delta E(C_\alpha + C_\beta + O)$ with $\Delta E(C_\alpha + C_\beta + 2O)$, because the resonance integral might not be the same in VIII and IX. However, it is very likely that IX has a larger delocalization energy than VIII.

The value of $\Delta E(C_\alpha + C_\beta + O)$ showed good agreement with the relative reactivity of the vinyl ether derivatives in the cationic copolymerization as shown in Table VI. The lower

reactivities of methyl trans-butenyl ether and trans-1,2-dimethoxyethylene compared to the calculated values may be due to the steric hindrance of the β -substituent. Therefore, VIII or IX is expected to represent the structure of the transition state in the propagation reaction in the cationic polymerization of the vinyl ether derivatives. This conclusion is also supported by the fact that steric hindrance of the β -substituent in the cationic polymerization of the vinyl ether derivatives is of minor importance.

Note

In this chapter, the transition state of propagation reaction in the cationic polymerization of a vinyl ether was discussed. The model proposed in this study was selected so as to concur with the experimental results regarding the relative reactivity of various vinyl ethers. Okuyama, et al.,²⁰ also deal with the same problem and they propose a model in which the chain end attacks both the α - and β -carbons of the olefinic bond simultaneously (Model VI in this study). The treatment in this chapter pursues faithfully the consistence with experimental results and Okuyama seems to attach importance to the concept of molecular orbital. Here, the author would like to lay stress specially on a point that the transition state in propagation reaction of a vinyl ether cannot be depicted as attack of the propagating end only on the β -carbon of double bond.

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Chapter 9

Molecular Properties and Reactivity of Vinyl Ethers and Styrene Derivatives

Introduction

Cationic polymerization of vinyl compounds belongs to the electrophilic addition reaction to carbon-carbon double bond like acid-catalyzed hydration and polar bromination of olefins. The nature of transition state of above-mentioned reactions is, however, very different to each other.^{1,2} This is manifested by studying the effects on these reactions, of substituent, catalyst, solvent, temperature, and so on. Vinyl ethers and styrene derivatives have been investigated in the field of cationic polymerization most frequently. So it will be of great interest to correlate the reactivity and the properties of vinyl ethers and styrene derivatives to have an insight into the nature of cationic polymerization. The properties of these compounds could be discussed in terms of nmr chemical shift, ionization potential, absorption in uv and visible regions, and basicity, which may have bearing on the reactivity in cationic polymerization.

In this chapter, the measurement of ^{13}C nmr spectra and the calculation of the electron density of the extended Hückel method are carried out for vinyl ethers, styrenes, and their α - and β -methyl substituted derivatives. From these results, the factors to determine the reactivity in cationic polymerization are discussed and a model for the transition state of cationic

polymerization is proposed.

Experimental

Materials

Ring-substituted phenyl vinyl ethers were prepared from ethylene dibromide and pertinent phenols by McElvain's method.³ Benzyl vinyl ether was synthesized by vinyl trans-etherification between isobutyl vinyl ether and benzyl alcohol.⁴ The synthetic methods of p-methoxystyrene, cis- β -methylstyrene, cis-anethole, ethyl isopropenyl ether, benzyl propenyl ether and phenyl propenyl ether are the same as in the previous chapters.^{5,6} As to ethyl vinyl ether, styrene, trans- β -methylstyrene and trans-anethole, commercial products were used after purification.

Measurement of ^{13}C Nmr Spectra

^{13}C nmr spectrum was taken at 15.09 MHz on a JNM-C-60HL spectrometer. The spectra were obtained at ambient temperature (23°C) using the neat liquids in an 8 mm diameter sample tube with a single scan by the $^{13}\text{C}\{-^1\text{H}\}$ noise decoupling method. Line positions were referenced against external benzene (65.0 ppm from carbon disulfide). Shifts are estimated to be accurate to within 0.2 ppm.

Calculation of Electron Densities

Electron density distribution of vinyl ethers and styrene derivatives was calculated using the extended Hückel methods.⁷ The following values were used for the Coulomb integrals: H(1s)-13.6, C(2s)-21.43, C(2p)-11.42, N(2s)-27.5, N(2p)-14.49,

Table I. ^{13}C nmr chemical shift of α - and β -carbons in methyl-substituted vinyl ethers and styrenes

	Unsubstituted		cis- β -Methyl		trans- β -Methyl		α -Methyl	
	C_β	C_α	C_β	C_α	C_β	C_α	C_β	C_α
Ethyl vinyl ether	107.6	41.6	79.0	47.7	80.5	46.3	112.6	28.6
Benzyl vinyl ether	105.5	41.8	91.5	47.7	94.0	46.7		
Phenyl vinyl ether	97.8	45.3	86.5	52.5	85.5	51.4		
Styrene	80.5	57.0	65.2	63.1	68.1	61.9	81.3	50.6
p-Methoxystyrene	82.3	57.2	68.6	63.5	70.3	63.0		

Table II. AOP of π -orbital in α - and β -carbons in methyl-substituted vinyl ethers and styrenes

	Unsubstituted		cis- β -Methyl		trans- β -Methyl		α -Methyl	
	C_{β}	C_{α}	C_{β}	C_{α}	C_{β}	C_{α}	C_{β}	C_{α}
Ethyl vinyl ether	1.1402	0.9159	1.0446	1.0436	1.0427	1.0415	1.2682	0.8384
Styrene	1.0545	0.9598	0.9556	1.0843	0.9509	1.0692	1.1672	0.8883

O(2s)-35.3, O(2p)-15.45, Cl(3s)-24.02, Cl(3p)-15.03. Bond lengths and angles used are almost the same as described in the previous chapter⁸.

Results and Discussion

Effect of α - and β -Methyl Substitution in Vinyl Ethers and Styrenes

Several equations have been proposed to correlate ^{13}C nmr chemical shift with electron density and bond order.⁹ From these equations it is generally accepted that the chemical shift is dependent mainly on the π -electron density and the increase in π -electron density brings about an upfield shift. Therefore, the shift is useful as a measure of electron density. ^{13}C nmr shifts of α - and β -carbons ($\delta_{\text{c}\alpha}$ and $\delta_{\text{c}\beta}$) in vinyl ethers, styrenes and their methyl-substituted derivatives are shown in Table I. The values for ethyl vinyl ether, styrene and p-methoxystyrene are reported in other references; re-determined values are shown in Table I. β -Methyl substitution induces a downfield shift of $\delta_{\text{c}\beta}$ and an upfield shift of $\delta_{\text{c}\alpha}$. Contrary to this, α -methyl substitution causes an upfield shift of $\delta_{\text{c}\beta}$ and a downfield shift of $\delta_{\text{c}\alpha}$. These results indicate that methyl substitution on a vinyl carbon leads to a decrease in the electron density of the substituted carbon and an increase in that of the other vinyl carbon. The magnitude of the change in chemical shift by methyl substitution is smaller in styrenes than that in vinyl ethers. A larger conjugation in styrenes may be responsible for this difference.

Calculations were made on the atomic orbital population (AOP) of π -orbital in α - and β -carbons of ethyl vinyl ether,

Table III. Reactivity of β -methyl-substituted vinyl ether and styrenes in cationic polymerization

Monomer 1	Monomer 2	Catalyst	Solvent	Temp, °C	r_1	r_2	$1/r_1$	Ref
Ethyl vinyl ether	Ethyl cis-propenyl ether	BF_3OEt_2	toluene	-78	0.35 ± 0.1	4.0 ± 0.5	2.86	10
"	Ethyl trans-propenyl ether	"	"	"	0.94 ± 0.1	0.94 ± 0.1	1.06	"
Benzyl vinyl ether	Benzyl cis-propenyl ether	"	CH_2Cl_2	"	0.41 ± 0.04	1.70 ± 0.08	2.44	11
"	Benzyl trans-propenyl ether	"	"	"	0.74 ± 0.07	0.85 ± 0.09	1.35	"
t-Butyl vinyl ether	t-Butyl cis-propenyl ether	"	toluene	"	2.2 ± 0.4	0.28 ± 0.08	0.46	12
Phenyl vinyl ether	Phenyl cis-propenyl ether	"	"	0	1.51 ± 0.20	0.14 ± 0.07	0.66	13
Styrene	cis- β -Methylstyrene	$\text{SnCl}_4 \cdot \text{TCA}$	$(\text{CH}_2\text{Cl})_2$	"	1.95 ± 0.1	0.03 ± 0.05	0.51	14
"	trans- β -Methylstyrene	"	"	"	1.4 ± 0.15	0.2 ± 0.1	0.71	"
p-Methoxy-styrene	cis-Anethole	"	toluene	-78	3.60 ± 0.23	0.00 ± 0.02	0.28	6
"	trans-Anethole	"	"	"	1.71 ± 0.09	0.01 ± 0.02	0.58	"

Table IV. Reactivity of α -methyl-substituted vinyl ether and styrene in cationic polymerization¹⁵

Monomer 1	Monomer 2	Catalyst	Solvent	Temp, °C	r_1	r_2	$1/r_1$
Ethyl vinyl ether	Ethyl isopropenyl ether	BF_3OEt_2	CH_2Cl_2	-78	0.13 ± 0.04	29.3 ± 3.5	7.7
Styrene	α -Methylstyrene	$\text{SnCl}_4 \cdot \text{TCA}$	"	"	0.25 ± 0.08	20.6 ± 3.5	4.0

styrene and their methyl-substituted derivatives. The results are shown in Table II (a part of them has already been calculated in a previous chapter⁸). When β -hydrogen is substituted for methyl group, the AOP of α -carbon increases and that of β -carbon decreases, and vice versa for α -methyl substitution. The results of calculation are consistent with the electron density from ^{13}C nmr.

In Table III are summarized the monomer reactivity ratio in cationic copolymerization of vinyl ethers and styrenes (M_1) with the corresponding β -methyl-substituted ones (M_2). The reciprocal of r_1 means the relative reactivity of M_2 to M_1 for a propagating end consisting of M_1 unit. The values of $1/r_1$ in ethyl and benzyl cis-propenyl ethers are obviously larger than unity. On the other hand, the β -methyl introduction to tert-butyl and phenyl vinyl ethers, styrene and p-methoxystyrene decreases the reactivity. In general, the β -methyl derivative of a bulky vinyl monomer has $1/r_1$ less than unity. Obviously β -methyl substitution gives rise to some steric hindrance, but still it leads to a slight increase in reactivity of less bulky vinyl compounds electronically.

In Table IV are represented the monomer reactivity ratios in the copolymerizations of ethyl vinyl ether and styrene (M_1) with their α -methyl-substituted derivatives (M_2).¹⁵ $1/r_1$ of ethyl vinyl ether is about 8, and that of styrene is about 4. As is clear from Tables III and IV, α -methyl substitution increases the reactivity more effectively than β -methyl substitution.

Structure and Reactivity of Vinyl Ethers and Ring-substituted Styrenes

^{13}C nmr chemical shifts of α - and β -carbons in alkyl vinyl

Table V. Reactivity in cationic polymerization and some properties of alkyl vinyl ethers

Alkyl	Relative polymeriz- ability ¹⁶	¹³ C nmr		AOP of π -orbital		IP		α -Alkoxyethyl cation	
		$\delta_{c\beta}$	$\delta_{c\alpha}$	C_{β}	C_{α}	obsd ¹⁸	calcd	AOP of C_{α}	Δ (TEE) from monomer
$(CH_3)_3C$	12.5	102.5	47.0	1.1556	0.9064	8.68	12.6972	0.3011	4.8338
$(CH_3)_2CH$	5.4	105.6	42.8	1.1461	0.9160	8.72	12.7139	0.3053	4.8132
CH_3CH_2	1.0	107.6	41.6	1.1402	0.9159	8.80	12.7999	0.2896	4.7752
CH_3	0.46	108.3	40.7	1.1400	0.9161	8.93	12.8104	0.2903	4.7764
$ClCH_2CH_2$	0.44	105.6	42.0	1.1403	0.9159	8.98	12.7963	0.2897	4.7754

ethers are shown in Table V. Hatada, et al., have also reported a similar result.¹⁷ The β -carbons in alkyl vinyl ethers resonate at much higher field than the carbons in ethylene ($\delta_c = 69.5$), and the signal shifted to higher field according to the alkyl group in the order, $(CH_3)_3C > (CH_3)_2CH \simeq ClCH_2CH_2 > CH_3CH_2 > CH_3$.

AOP of π -orbital in alkyl vinyl ethers are calculated assuming s-trans conformation. The order of AOP in α - and β -carbons proved to be opposite to that expected from ^{13}C nmr. This may be due to the influence of excitation energy of the compounds on the chemical shift or the wrong assumption of a single conformer (s-trans form) in the calculation. In consequence, the effect of the alkyl group on the electron density in alkyl vinyl ethers is not firmly established. Apart from this ambiguity, the difference of electron density between α - and β -carbons is very large in alkyl vinyl ethers.

The stability of the carbocation formed by olefin protonation is definitely one of the important factors controlling olefin reactivity. The following values have been calculated as the measures of the stability of carbocation: ionization potential (IP), AOP of π -orbital in a carbocation, and the difference in total electron energies (TEE) of a monomer and the carbocation derived from it. Carbocations were depicted as protonated form of each monomer. In Table V are cited the experimental values of IP of vinyl ethers reported by Ledwith, et al.¹⁸ Both experimental and calculated IP values indicate that tert-butyl vinyl ether is protonated most easily. No rule was derived from AOP of α -carbon. TEE of carbocation is more negative than that of the original monomer. The difference between them is the greatest in tert-butyl vinyl ether, which means that the rela-

tive stability of carbocation against the starting olefin is the largest in tert-butyl vinyl ether.

The relative reactivity of alkyl vinyl ethers ($1/r_1$; M_1 : ethyl vinyl ether) in cationic polymerization is shown in Table V.¹⁶ A similar sequence is obtained by Yuki, et al.¹⁹ Taking ethyl vinyl ether as standard, the relative reactivity of tert-butyl vinyl ether is 12.5 and the greatest, and that of 2-chloroethyl vinyl ether is 0.44. Apparently, the more electron-donating the alkyl group, the greater the reactivity.

The relative reactivity in cationic polymerization,²⁰ ^{13}C nmr chemical shift, AOP of π -orbital of ring-substituted phenyl vinyl ethers are shown in Table VI. In phenyl vinyl ethers, the greater the relative reactivity of a monomer, the greater the $\delta_{\text{c}\beta}$. The $\delta_{\text{c}\beta}$'s are small as compared with those of alkyl vinyl ethers. AOP of π -orbital is almost unaffected by ring substitution. Also, IP and TEE were little affected by the nature of ring substituent.

The computation of AOP of para-substituted styrenes were carried out, the data being shown in Table VII. The relative reactivity demonstrates a very large influence of substituent; for example, p-dimethylaminostyrene is 170 times as reactive as styrene. The larger the $\delta_{\text{c}\beta}$, the more reactive the monomer. The AOP of β -carbon becomes greater when a substituent becomes more electron-donating. In this case, changes in $\delta_{\text{c}\beta}$ and $\delta_{\text{c}\alpha}$ accord with those in AOP of C_β and C_α , respectively. IP and the values for carbocation indicate that a stable carbocation is produced from the monomer with an electron-donating substituent. The calculated values of p-chlorostyrene is peculiar, probably due to the inadequate parameters. When styrenes are compared

Table VI. Reactivity in cationic polymerization and some properties of para-substituted phenyl vinyl ethers

Substi- tuent	Relative polymeriz- ability ²⁰	¹³ C nmr		AOP of π -orbital		IP calcd ^{a)}	α -Phenoxyethyl cation	
		$\delta_{C\beta}$	$\delta_{C\alpha}$	C_{β}	C_{α}		AOP of C_{α}	$\Delta(\text{TEE})$ from monomer
CH ₃ O	2.38	99.5	44.0	1.1284	0.9231	12.9334	0.2884	4.7466
CH ₃	1.82	98.8	44.8	1.1284	0.9231	12.9354	0.2884	4.7464
H	1.00	97.8	45.3	1.1281	0.9231	12.9678	0.2869	4.7442
Cl	0.278	96.9	45.4	1.1285	0.9231	12.9281	0.2890	4.7442

a) The values of π -orbital in vinyl group.

Table VII. Reactivity in cationic polymerization and some properties of para-substituted styrenes

Substi- tuent	Relative polymeriz- ability ²¹	¹³ C nmr ²²		AOP of π -orbital		IP		Styryl cation	
		$\delta_{c\beta}$	$\delta_{c\alpha}$	C_{β}	C_{α}	obsd ²³	calcd	AOP of C_{α}	$\Delta(\text{TEE})$ from monomer
$(\text{CH}_3)_2\text{N}$	171	85.3	56.4	1.0792	0.9576	7.55 ^{a)}	12.0507	0.4894	5.1921
CH_3O	19.8	82.3	57.2	1.0742	0.9578	7.92	12.1581	0.4692	5.1694
CH_3	1.81	79.7	56.2	1.0710	0.9582	8.20	12.1666	0.4649	5.1461
H	1.00	80.5	57.0	1.0545	0.9598	8.47	12.3596	0.4227	5.0603
Cl	0.401	78.7	59.1	1.0747	0.9579	8.46	12.1270	0.4749	5.1663

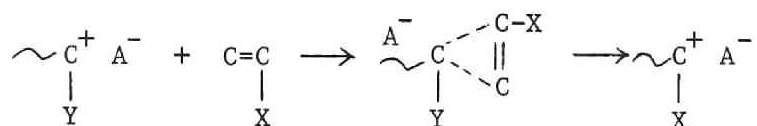
a) The value for p-aminostyrene.

with phenyl vinyl ethers, one will notice that the substituent effect on the relative reactivity is much greater with the former, but that on chemical shift is about the same. According to Olah, et al.,²⁴ the chemical shift of α -carbon in styryl cations depends on the substituent much more strongly than that of β -carbon in styrenes does.

Some Considerations on Reaction Mechanism of Vinyl Ethers and Styrenes

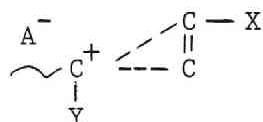
The nucleophilicity is an important factor to determine the reactivity of a monomer in cationic polymerization. It could be inferred from the electron density of the β -carbon. $\delta_{c\beta}$ and AOP of β -carbon in vinyl ethers are much greater than those in styrenes (e.g., ethyl vinyl ether, $\delta_{c\beta}$ 107.6, AOP 1.1402; styrene, $\delta_{c\beta}$ 80.5, AOP 1.0545). This leads to the high reactivity of vinyl ethers in electrophilic reactions. On the other hand, the observed value of IP of styrenes is smaller than that of vinyl ethers, but AOP of α -carbon of styryl cations is larger than expected. This means that phenyl group stabilizes a carbocation as effectively as alkoxy group. This explains why styrenes have a considerable reactivity in cationic polymerization.

Propagation reaction could be divided into two stages:²⁵



At the former stage, a monomer and a propagating end produce a π -complex. This stage is controlled by the nucleophilicity of

a monomer and may be correlated with the basicity and solvating power of a monomer. The latter stage is governed by the stability of an ion formed. The stability will be assessed by IP of a monomer, the difference in TEE's of a monomer and the carbocation and so forth. When the first step is rate-determining, α - and β -methyl substitutions will influence the reactivity equally. If the latter step is rate-determining, α -methyl group will play a greater role than β -methyl group, since a β -substituent hardly contributes to the stabilization of an ion. In fact, β -methyl substituent increases the reactivity, but α -methyl substituent increases the reactivity more strongly. So, both stages should be taken into account. From these considerations, a following model is proposed for the transition state of cationic polymerization:



A similar model is proposed for the polar bromine addition to styrenes.²⁶

Vinyl ethers are more basic and have a stronger solvating power than styrenes. Therefore, the former will form the π -complex more easily. As the dissociation of a propagating ion pair is needed at the first step, the reactivity of styrenes relative to vinyl ethers will increase under the conditions in which a counterion dissociates easily. This influence has been supported by the studies described in the previous chapter.²⁷

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PART IV

SALT EFFECT ON POLYMERIZATION RATE AND ON MOLECULAR
WEIGHT DISTRIBUTION OF THE POLYMER

Chapter 10

Salt Effect in the Polymerization by Various Catalysts

Introduction

It is well known that neutral salts can affect the rates of ionic reactions in solution. The results have been interpreted principally on the basis of the change in ionic strength and the mass-law effect. Ingold and his collaborators¹ have carried out an extensive investigation of the effect of salts on substitution reactions, especially on solvolysis. Winstein, et al.,² found both normal and special salt effects in solvolysis on the basis of their detailed experimental results. On the other hand, there have been few papers on the salt effect in electrophilic addition to unsaturated compounds, which is intimately related to cationic polymerization. Recently, several studies have been reported on the salt effect in electrophilic addition.³⁻⁵ For example, in a series of studies on the halogenation of olefins, it was found that a neutral salt acted not only as an electrolyte but also as a nucleophile.^{3,4}

In view of the nature of ionic polymerizations, salt effects are to be anticipated. In practice, it has been confirmed that a common ion depresses the dissociation of an ion pair and decreases the rate of propagation in anionic polymerization.^{6,7} In cationic polymerization there have been two papers^{8,9} on salt effects, in which it was concluded that the added salt depresses the dissociation of an ion pair similar to that in

anionic polymerization, since the common salt lowers both the reaction rate and the molecular weight of the polymer formed.

However, the function of an added salt as a nucleophile has not been considered in cationic polymerization, although it has been observed in electrophilic addition reactions. Therefore, in order to elucidate the functions of added salts in cationic polymerization, the following effects were examined: (1) the influence of tetra-n-butylammonium salts on the cationic polymerization of styrene catalyzed by acetyl perchlorate and metal halides, and (2) the effect of tetra-n-butylammonium perchlorate on the composition of a copolymer obtained by cationic copolymerization of 2-chloroethyl vinyl ether (CEVE) with α -methylstyrene (α MS). The results were mainly interpreted in terms of counterion exchange and a terminating function of the added tetra-n-butyl ammonium salts.

Experimental

Materials

Three salts, tetra-n-butylammonium perchlorate ($n\text{-Bu}_4\text{NClO}_4$), tetra-n-butylammonium fluoroborate ($n\text{-Bu}_4\text{NBF}_4$) and tetra-n-butylammonium iodide ($n\text{-Bu}_4\text{NI}$) were synthesized by a procedure (eq 1) similar to Fujinaga's method:¹⁰

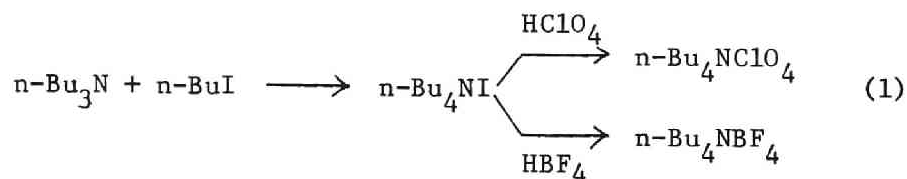


Table I shows the composition and melting point of the salts

Table I. Composition and melting point of tetra-n-butylammonium salts

	Composition found (calcd)				Mp, °C	
	H, %	C, %	Cl or I, %	O, %	Obsd	Ref ¹¹
n-Bu ₄ NClO ₄	10.58 (10.62)	56.28 (56.25)	10.48 (10.38)	18.55 (18.74)	217	213
n-Bu ₄ NBF ₄	11.33 (11.03)	58.18 (58.42)	—	—	163	161.8
n-Bu ₄ NI	9.84 (9.83)	51.87 (52.07)	34.63 (34.39)	—	147	148

obtained. As seen from Table I, the purity of the salts was more than 99.8%.

The synthesis and purification of catalysts and monomers were performed by the same methods described in previous chapters.^{12,13}

Procedures

Polymerization was carried out in a flask fitted with a double cap and under a nitrogen atmosphere. Salt solutions were added to the monomer solutions through the double cap by a syringe, and polymerization was then initiated by addition of the catalyst solution.

Rates of polymerization were determined by measuring concentrations of unreacted monomer by gas chromatography. A first-order plot of monomer consumption was linear in all cases. Polymer was precipitated in a large quantity of methanol, washed, filtered, and dried. In the case of polymers which are soluble in methanol, the polymers were purified by freeze-drying after the evaporation of volatile materials.

Copolymer compositions were determined by measuring the residual monomer concentrations by gas chromatography.

Limiting viscosity numbers $[\eta]$ were determined in benzene solution at 30°C.

Results and Discussion

Effect of Tetra-n-butylammonium Salts on the Cationic Polymerization of Styrene

Styrene was polymerized at 0°C by various catalysts with or without the tetra-n-butylammonium salt. In all cases a constant

initial concentration of styrene (1.00 mol/l) was used. In the procedure described above, the reaction system contained a small amount of water (ca. 1 mmol/l). No polymerization occurred in the presence of the tetra-*n*-butylammonium salt without the addition of an acidic catalyst.

Effect of $n\text{-Bu}_4\text{NClO}_4$ on the Cationic Polymerization of Styrene with Various Catalysts

To clarify the effect of a neutral salt on the rate of cationic polymerization of styrene, styrene was polymerized in methylene chloride solution with various concentrations of added salt. $n\text{-Bu}_4\text{NClO}_4$ was used as the salt, and acetyl perchlorate (AcClO_4), SnCl_4 , $\text{SnCl}_4 \cdot \text{TCA}$ (TCA: trichloroacetic acid; 1:1 mole ratio) and boron trifluoride diethyl etherate (BF_3OEt_2) as catalysts. AcClO_4 was the only catalyst having the same anion as the added salt.

As Figure 1 shows, the rates of polymerization at low concentration of $n\text{-Bu}_4\text{NClO}_4$ increased to a maximum value in polymerization catalyzed by metal halides. At higher concentrations of $n\text{-Bu}_4\text{NClO}_4$ the rates of polymerization decreased. On the other hand, when AcClO_4 was used as catalyst, a small amount of $n\text{-Bu}_4\text{NClO}_4$ caused a rapid reduction in rate and then the rate decreased gradually with increasing the concentration of the salt. The behavior of AcClO_4 - $n\text{-Bu}_4\text{NClO}_4$ system is very similar to that of the HClO_4 - $n\text{-Bu}_4\text{NClO}_4$ system, as reported by Pepper.^{8,9}

Figure 2 shows the limiting viscosity numbers $[\eta]$ of the resultant polymers. $[\eta]$ was decreased significantly by the addition of small amounts of salt and gradually decreased further with increasing of the concentration of the salt, approaching a constant value irrespective of the catalyst used.

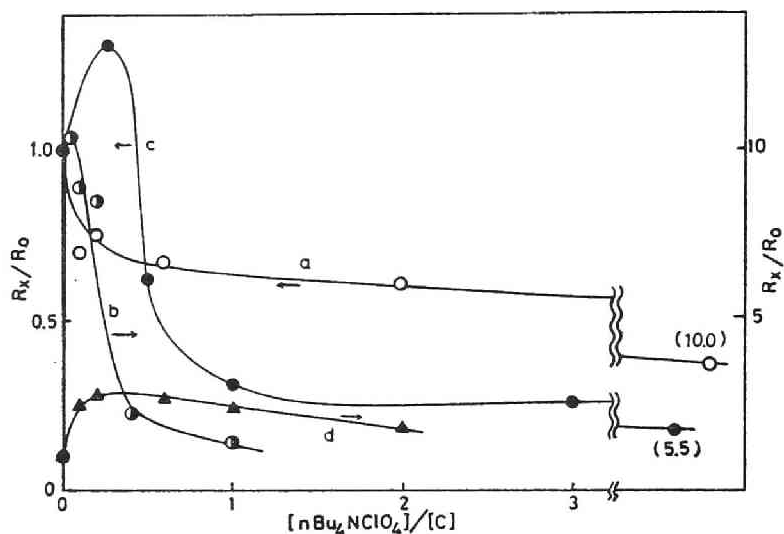


Figure 1. Effect of $n\text{-Bu}_4\text{NClO}_4$ on the rate of polymerization initiated by various catalysts in methylene chloride at 0°C and $[\text{M}]_0 = 1.00$ mole/l. a(o), $[\text{AcClO}_4]_0$ 0.50 mmol/l, $R_0 = 1.57\%/ \text{min}$; b(\bullet), $[\text{SnCl}_4]_0$ 5.0 mmol/l, $R_0 = 0.95\%/ \text{min}$; c(\bullet), $[\text{SnCl}_4 \cdot \text{TCA}]_0$ 1.0 mmol/l, $R = 4.61\%/ \text{min}$; d(\blacktriangle), $[\text{BF}_3\text{OEt}_2]_0$ 5.0 mmol/l, $R = 0.35\%/ \text{min}$.

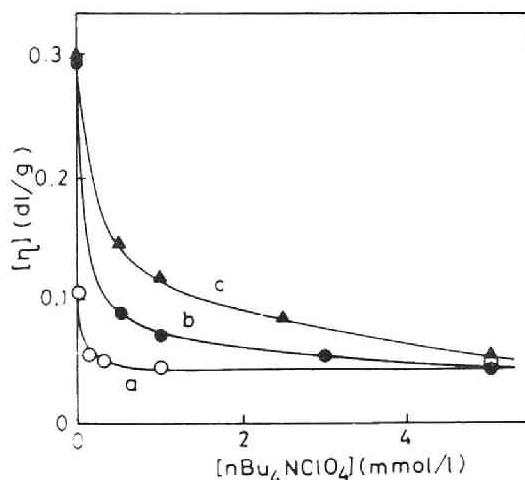


Figure 2. Effect of $n\text{-Bu}_4\text{NClO}_4$ on the limiting viscosity numbers of the polymer obtained by various catalysts (Polymerization conditions are the same as in Figure 1). a(o), AcClO_4 ; b(\bullet), SnCl_4 , c(\blacktriangle), BF_3OEt_2 .

Effect of $n\text{-Bu}_4\text{NClO}_4$ on the Cationic Polymerization of Styrene in Various Solvents

The acceleration effect of $n\text{-Bu}_4\text{NClO}_4$ on the polymerization of styrene initiated by SnCl_4 is shown in Figure 3. A small

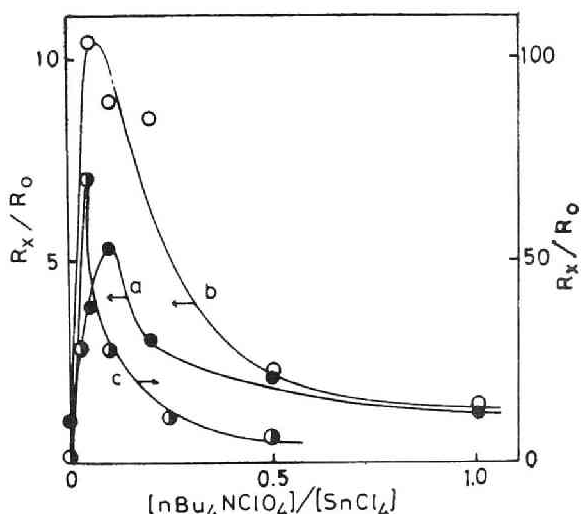


Figure 3. Effect of $n\text{-Bu}_4\text{NClO}_4$ on the rate of polymerization catalyzed by SnCl_4 in various solvents at 0°C and $[\text{M}]_0 = 1.00$ mol/l. a(\bullet), nitrobenzene, $[\text{C}]_0$ 5.0 mmol/l, $R_0 = 9.52\%/min$; b(o), CH_2Cl_2 , $[\text{C}]_0$ 5.0 mmol/l, $R_0 = 0.95\%/min$; c(\bullet), $\text{CH}_2\text{Cl}_2/\text{benzene}$ (3/1 vol ratio), $[\text{C}]_0$ 10.0 mmol/l, $R_0 = 0.14\%/min$.

amount of $n\text{-Bu}_4\text{NClO}_4$ increased the rate of polymerization irrespective of the nature of the solvent, and further addition of the salt decreased the rate. A discussion of the relationship between the nature of the solvent and variation in rate is difficult since the amount of water, as cocatalyst, was not controlled.

On the other hand, the effect of $n\text{-Bu}_4\text{NClO}_4$ on the polymerization of styrene initiated by AcClO_4 could be compared in

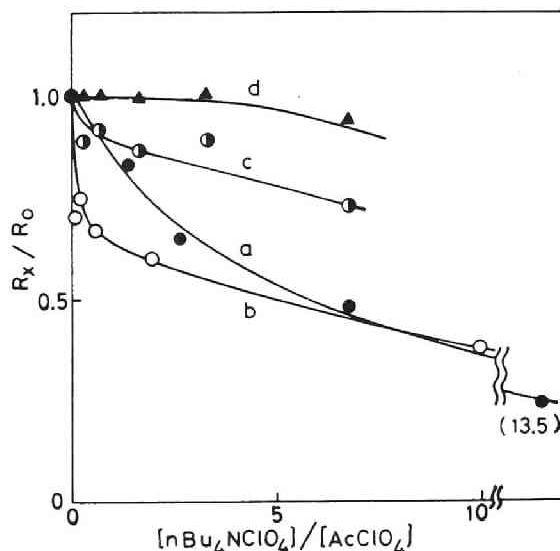


Figure 4. Effect of $n\text{-Bu}_4\text{NClO}_4$ on the rate of polymerization catalyzed by AcClO_4 in various solvents at 0°C and $[\text{M}]_0 = 1.00$ mol/l. a(\bullet), nitrobenzene, $[\text{C}]_0$ 0.37 mmol/l, $R_0 = 9.58\%/ \text{min}$; b(o), CH_2Cl_2 , $[\text{C}]_0$ 0.50 mmol/l, $R_0 = 1.57\%/ \text{min}$; c(\bullet), $\text{CH}_2\text{Cl}_2/\text{benzene}$ (3/1 vol ratio), $[\text{C}]_0$ 1.48 mmol/l, $R_0 = 2.22\%/ \text{min}$; d(\blacktriangle), $\text{CH}_2\text{Cl}_2/\text{benzene}$ (1/3 vol ratio), $[\text{C}]_0$ 1.48 mmol/l, $R_0 = 0.23\%/ \text{min}$.

various solvents. As shown in Figure 4, the depression of the rate of polymerization due to the addition of the salt decreased with decreasing polarity of the solvent, except for the remarkable decrease of the rate by an addition of a small amount of the salt in methylene chloride.

$[\eta]$ of the polymer decreased to a constant value in each solvent as shown in Figure 5, and $[\eta]$ of polymer produced in a polar solvent was higher than that produced in a nonpolar solvent.

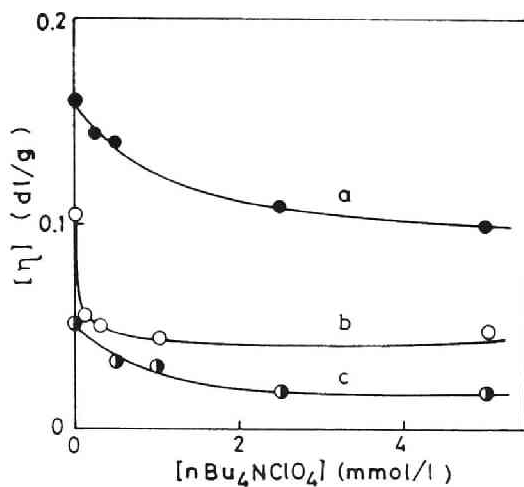


Figure 5. Effect of $n\text{-Bu}_4\text{NClO}_4$ on the limiting viscosity numbers of the polymer obtained by AcClO_4 (Polymerization conditions are the same as in Figure 4). a(●), nitrobenzene; b(○), CH_2Cl_2 ; c(●), CH_2Cl_2 /benzene (3/1 vol ratio).

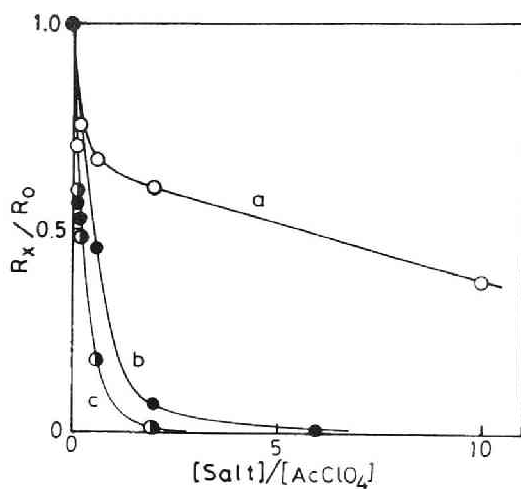


Figure 6. Effect of various tetra- n -butylammonium salts on the rate of polymerization catalyzed by AcClO_4 in methylene chloride at 0°C , $[\text{M}]_0 = 1.00 \text{ mol/l}$ and $[\text{C}]_0 = 0.50 \text{ mmol/l}$. a(○), $n\text{-Bu}_4\text{NClO}_4$, $R_0 = 1.57\%/ \text{min}$; b(●), $n\text{-Bu}_4\text{NBF}_4$, $R_0 = 1.99\%/ \text{min}$; c(●), $n\text{-Bu}_4\text{NI}$, $R_0 = 1.69\%/ \text{min}$.

Effect of varying the negative ion of the salt

The influence of negative ions was examined by using tetra-*n*-butylammonium salts having various negative ions. Styrene was polymerized by AcClO_4 or SnCl_4 in methylene chloride in the presence of $n\text{-Bu}_4\text{NClO}_4$, $n\text{-Bu}_4\text{NBF}_4$, or $n\text{-Bu}_4\text{NI}$. $n\text{-Bu}_4\text{NBF}_4$ and $n\text{-Bu}_4\text{NI}$ strikingly decreased the rate of polymerization catalyzed by AcClO_4 and by SnCl_4 (Figures 6 and 7.). $n\text{-Bu}_4\text{NI}$ retarded polymerization more strongly than $n\text{-Bu}_4\text{NBF}_4$ did.

The presence of $n\text{-Bu}_4\text{NBF}_4$ or $n\text{-Bu}_4\text{NI}$ decreased the rate of polymerization also in a mixture of methylene chloride and benzene, and the retarding effect of the salt was smaller in a nonpolar solvent than in a polar solvent.

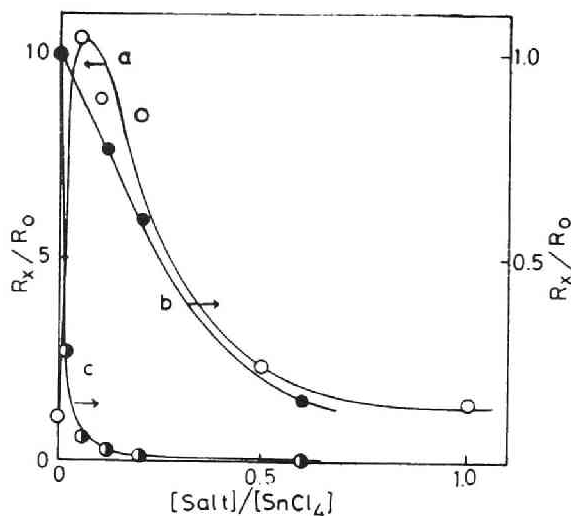


Figure 7. Effect of various tetra-*n*-butylammonium salts on the rate of polymerization catalyzed by SnCl_4 in methylene chloride at 0°C , $[\text{M}]_0 = 1.00$ mol/l and $[\text{C}]_0 = 5.0$ mmol/l. a(o), $n\text{-Bu}_4\text{NClO}_4$, $R_0 = 0.95\%/min$; b(●), $n\text{-Bu}_4\text{NBF}_4$, $R_0 = 0.99\%/min$; c(○), $n\text{-Bu}_4\text{NI}$, $R_0 = 0.90\%/min$.

Discussion

It is well known that a compound forming a proton or carbocation acts as a cocatalyst in the polymerization of styrene catalyzed by a metal halide. However, the accelerating effect by neutral salt, such as $n\text{-Bu}_4\text{NClO}_4$, has not been observed in the cationic polymerization of styrene.

The neutral salt effect on the rates of ionic reactions in solution is mainly a result of the change in ionic strength and mass-law effect, as described in the introduction. Furthermore, it has often been observed that neutral salts add directly to olefins in an electrophilic addition reaction.³⁻⁵ Therefore, three possible effects of the salt on the polymerization of styrene were considered:

(i) Change in ionic strength. The termination reaction is a reaction between ionic species, while initiation and propagation are ion-dipolar molecule reactions. Therefore, if the change in ionic strength influences the reaction rate, the overall rate should increase with increasing ionic strength, accordingly by addition of salt. However, in the system with AcClO_4 as catalyst, $n\text{-Bu}_4\text{NClO}_4$ did not increase the rate of polymerization and the effect of the salt depended on the nature of catalysts employed. Therefore, the change in rate due to change in ionic strength may be neglected in comparison with that of some other salt effect. This agreed with the conclusion of George, et al.¹⁴

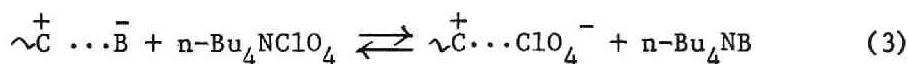
(ii) Change in dissociation by a common ion. It was observed by Pepper that $n\text{-Bu}_4\text{NClO}_4$ decreased not only the rate of polymerization but also the molecular weight of the polymer in the polymerization of styrene with perchloric acid.^{8,9} From this it was suggested that the addition of $n\text{-Bu}_4\text{NClO}_4$ prevented the

dissociation of the propagating ion and consequently the propagation through free ions. In the present work the addition of $n\text{-Bu}_4\text{NClO}_4$ to a polymerization system catalyzed by AcClO_4 also decreased the rate of polymerization and the molecular weight of a resultant polymer. This result also seems to be interpretable by the explanation proposed by Pepper.

However, addition of the salt in concentrations of more than a half mole of a catalyst lowered the rate of polymerization irrespective of the nature of a catalyst. Therefore, the decrease in a rate of polymerization due to the addition of $n\text{-Bu}_4\text{NClO}_4$ must be explained by a termination or transfer reaction of a propagating chain by $n\text{-Bu}_4\text{NClO}_4$, the mechanism of which is not clear yet.

(iii) Exchange of a counterion at the growing chain end with the salt. $n\text{-Bu}_4\text{NClO}_4$ having no common ion increased the rate of polymerization catalyzed by SnCl_4 , $\text{SnCl}_4 \cdot \text{TCA}$ or $\text{BF}_3 \cdot \text{OEt}_2$. It was observed that the cationic polymerization of styrene was accelerated by tetracyanoethylene from which a proton or carbocation was not produced.¹⁵ This was explained by the stabilization of a counterion in a growing chain end due to complexing with tetracyanoethylene, a strong electrophile. However, such electrophilic behavior is improbable about $n\text{-Bu}_4\text{NClO}_4$.

In electrophilic addition to olefins, an anion produced from a neutral salt adds to an olefin.³⁻⁵ In the same way, it is easily anticipated that the anion of a salt interacts with a propagating carbocation in cationic polymerization. In the latter case, as the anion may be more stable than that in the addition reaction to an olefin, the anion will not add to the propagating carbocation, but rather will form an ion pair; in consequence, the polymerization proceeds with an exchanged counterion (eq 3).



Here, if the rate of a growing carbocation having ClO_4^- as counterion is greater than that having B^- as the counterion, the addition of $\text{n-Bu}_4\text{NClO}_4$ will increase the rate of polymerization. The polymerization with SnCl_4 , $\text{SnCl}_4 \cdot \text{TCA}$ or BF_3OEt_2 in the presence of a small amount of $\text{n-Bu}_4\text{NClO}_4$ can be explained by this mechanism.

On the other hand, the presence of $\text{n-Bu}_4\text{NBF}_4$ or $\text{n-Bu}_4\text{NI}$ decreased the rate of polymerization. This may be due to the slow polymerization with BF_4^- or I^- as a counterion.

The occurrence of counterion exchange was also supported on the basis of the molecular weights of the polymers. The molecular weights of the polymers approached a constant value in the presence of large concentrations of $\text{n-Bu}_4\text{NClO}_4$, irrespective of the catalyst. This is attributed to the fact that the counterion in a growing chain end is completely exchanged by ClO_4^- in the presence of a large amount of $\text{n-Bu}_4\text{NClO}_4$.

It has been reported that in the living anionic polymerization of styrene an added salt and a propagating chain end interacted metathetically and the counterion was exchanged,¹⁶ that is, the exchange of a counterion occurred when NaBPh_4 was added to living polystyrene having K^+ counterion, as KBPh_4 was less soluble than NaBPh_4 .

The author believe that the present work provided the first example of an exchange reaction of counterion in cationic polymerization.

Effect of $n\text{-Bu}_4\text{NClO}_4$ on the Cationic Copolymerization
of CEVE with αMS

To confirm the occurrence of counterion exchange in cationic polymerization, the effect of an addition of the salt on the monomer reactivity ratios in copolymerization was examined. Copolymerization of CEVE with αMS produced copolymers the composition of which is very sensitive to the catalyst employed, i.e., to the nature of the counterion.^{12,13} It is expected, therefore, that the copolymer composition will be changed by the addition of the salt, if the counterion is changed by the addition of a salt.

Effect of $n\text{-Bu}_4\text{NClO}_4$ on Copolymer Composition

The compositions of copolymers of CEVE with αMS obtained with SnCl_4 and AcClO_4 as catalysts were very different, as Figure 8 shows. When three times as much $n\text{-Bu}_4\text{NClO}_4$ was added to a polymerizing system catalyzed by SnCl_4 ($[n\text{-Bu}_4\text{NClO}_4] = 3[\text{SnCl}_4]$), the copolymer composition curve became identical with that obtained with AcClO_4 catalyst as shown in Figure 8. On the other hand, no change in copolymer composition was observed when trichloroacetic acid was added to the same system.

The same effect of $n\text{-Bu}_4\text{NClO}_4$ on copolymer composition was also found in polymerizations in a mixed solvent of methylene chloride and toluene. As Figure 9 shows, the addition of one and half times as much $n\text{-Bu}_4\text{NClO}_4$ as SnCl_4 changed the copolymer composition obtained by SnCl_4 catalyst to that obtained with AcClO_4 .

On the other hand, in the copolymerization catalyzed by AcClO_4 , addition of ten times as much $n\text{-Bu}_4\text{ClO}_4$ as catalyst

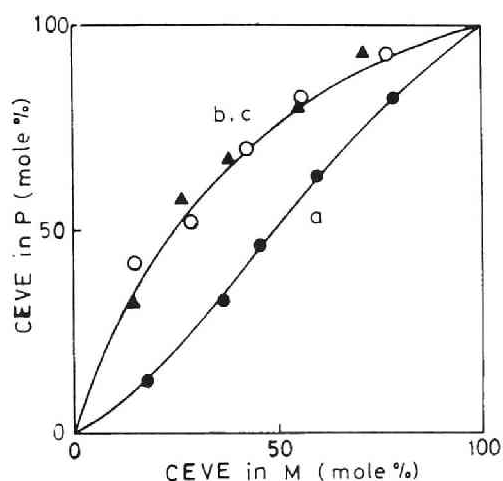


Figure 8. Salt effect on copolymer compositions in the copolymerization of CEVE with α MS in methylene chloride at -78°C and $[\text{M}]_0 = 0.50 \text{ mol/l}$. a(\bullet), $[\text{SnCl}_4]_0 = 3.0 \text{ mmol/l}$; b(o), $[\text{AcClO}_4]_0 = 0.22 \text{ mmol/l}$; c(\blacktriangle), $[\text{SnCl}_4]_0 = 1.0 \text{ mmol/l}$, $[\text{n-Bu}_4\text{NClO}_4] = 3.0 \text{ mmol/l}$.

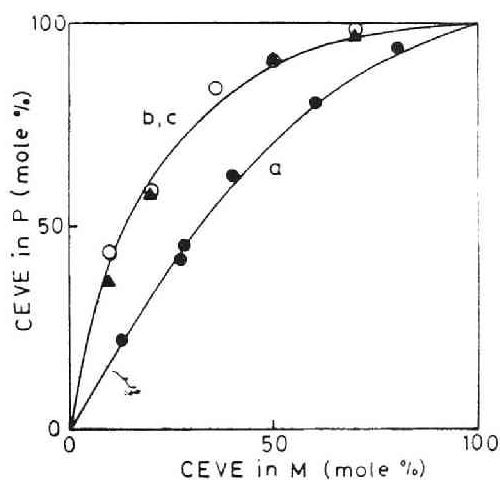


Figure 9. Salt effect on copolymer compositions in the copolymerization of CEVE with α MS in methylene chloride/toluene solution (1/3 vol ratio) at -78°C and $[\text{M}]_0 = 0.50 \text{ mol/l}$. a(\bullet), $[\text{SnCl}_4] = 5.0 \text{ mmol/l}$; b(o), $[\text{AcClO}_4] = 0.37 \text{ mmol/l}$; c(\blacktriangle), $[\text{SnCl}_4] = 2.0 \text{ mmol/l}$, $[\text{n-Bu}_4\text{NClO}_4] = 3.0 \text{ mmol/l}$.

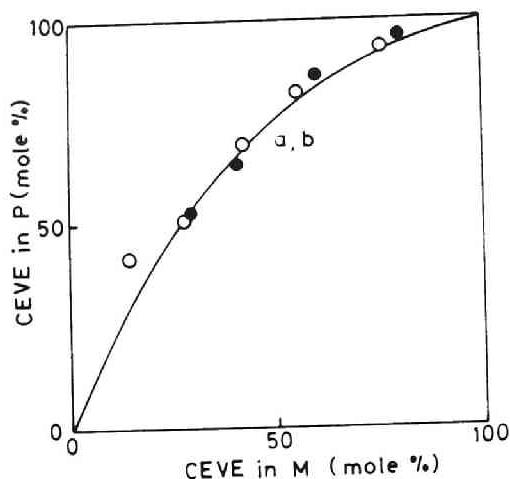


Figure 10. Salt effect on copolymer compositions in the copolymerization of CEVE with α MS in methylene chloride at -78°C and $[\text{M}]_0 = 0.50 \text{ mol/l}$. a(○), $[\text{AcClO}_4] 0.22 \text{ mmol/l}$; b(●), $[\text{AcClO}_4] 0.22 \text{ mmol/l}$, $[\text{n-Bu}_4\text{NClO}_4] 3.0 \text{ mmol/l}$.

produced no effect in the copolymer composition (Fig. 10).

Discussion

The presence of large concentration of common ion does not affect the copolymer composition as shown in Figure 10. Meanwhile, the coincidence of the composition curves b and c in Figure 8 establishes that the counterions are identical, that is, ClO_4^- in both systems. The amount of $\text{n-Bu}_4\text{ClO}_4$ added to the copolymerization system appears to be sufficient to cause complete exchange of counterion, since the molecular weight of a polymer obtained under these conditions was almost identical with that obtained by AcClO_4 (Figure 2).

At the present time, it is not clear whether a counterion is exchanged during the propagation step or before propagation

directly by the reaction of catalyst and the salt. However, it is concluded that the exchange of a counterion takes place in the polymerization of styrene and in the copolymerization of CEVE with α MS.

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Chapter 11

Salt Effect in the Polymerization by Iodine

Introduction

There have recently been several attempts to elucidate the mechanism of ionic polymerization by changing a counterion itself or the state of a counterion during polymerization. These are classified into two types of investigation. In one of them the additives which can solvate a counterion are employed. In this connection, there are papers by Panayotov and his colleagues^{1,2} in the field of cationic polymerization, and by Szwarc³ and Tomoi⁴ in anionic polymerization. The other investigation involves studies on the influence of added salts in the field of kinetics in cationic polymerization.⁵⁻⁹ Schulz¹⁰ reports on the common-salt effect and Hsieh¹¹ on the uncommon-salt effect in anionic polymerization.

In the investigation of the previous chapter,⁹ it was found that added salts affect both polymerization rate and molecular weight of the polymer in the cationic polymerization of styrene. The phenomena were attributed to the exchange of a counterion and the chain-transfer reaction.

In this chapter the salt effect is studied in the cationic polymerization of a vinyl ether and a styrene derivative using iodine as a catalyst. There are two reasons why iodine is used as a catalyst: (a) the possibility that an added salt may work as a cocatalyst is avoided, for iodine does not need a cocatalyst, and (b) as iodine is a relatively weak catalyst, an increase

in the polymerization rate by adding a certain salt would be expected.

Experimental

Materials

The synthesis and purification of the salts used, i.e., tetra-n-butylammonium perchlorate ($n\text{-Bu}_4\text{NClO}_4$), tetra-n-butylammonium fluoroborate ($n\text{-Bu}_4\text{NBF}_4$), and tetra-n-butylammonium iodide ($n\text{-Bu}_4\text{NI}$) are described elsewhere.⁹ 2-Chloroethyl vinyl ether (CEVE), p-methoxystyrene (pMOS)¹² and the solvents, methylene chloride, benzene, and nitrobenzene were purified in the usual manner. Iodine (E. Merck, resublimed reagent) was used without further purification.

Procedures

Details of the procedures are similar to those described previously.⁹ Polymerization was carried out at 0°C using iodine with 1.0 mmol/l concentration mainly in methylene dichloride. Acetyl perchlorate (AcClO_4) and acetyl fluoroborate (AcBF_4) were applied as catalysts for comparison with iodine. The polymerization rate was determined by measuring the monomer consumption by gas chromatography. The poly(2-chloroethyl vinyl ether) (poly(CEVE)) obtained was precipitated in a large amount of methanol-water mixture (vol ratio, 3:1). Poly(p-methoxystyrene) (poly(pMOS)) was precipitated in methanol. Viscosity number, η_{sp}/c , of the polymers was measured in benzene at 30°C.

Results

The Effect of the Salts on Polymerization Rate

Iodine is a comparatively weak catalyst for cationic polymerization, with which CEVE and pMOS polymerize at 0°C at a slow rate as shown in Figure 1. No induction period is observed

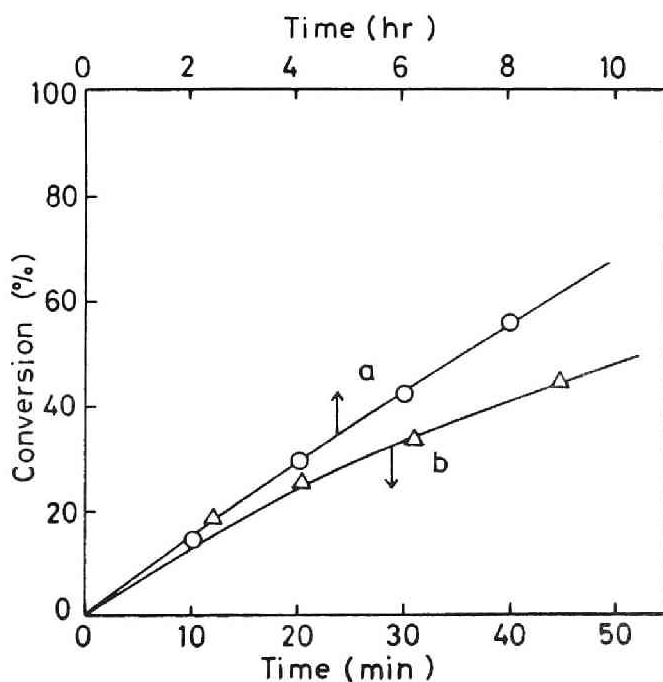


Figure 1. Time-conversion curves in the polymerization of CEVE and pMOS catalyzed by iodine in methylene chloride at 0°C: $[M]_0$, 0.50 mol/l; $[C]_0$, 1.0 mmol/l; a(o), CEVE; b(Δ), pMOS.

in the polymerizations. The polymerization rate was calculated at 40-50% conversion assuming monomer concentration to have a first-order effect; the polymerization rate of CEVE was 0.17

%/min and that of pMOS 1.4%/min.

In the presence of 10 mmol/l of $n\text{-Bu}_4\text{NClO}_4$, $n\text{-Bu}_4\text{NBF}_4$ or $n\text{-Bu}_4\text{NI}$ instead of iodine in the polymerization system, neither monomer was consumed after 10 hr. This confirms that the salts are not capable of initiating polymerization.

It was concluded in the previous chapter⁹ that the presence of a salt gives rise to the exchange of a counterion. Then, polymerization may proceed taking ClO_4^- and BF_4^- as a counterion when $n\text{-Bu}_4\text{NClO}_4$ and $n\text{-Bu}_4\text{NBF}_4$ are added, respectively. Therefore, the polymerization rate was investigated applying AcClO_4 and AcBF_4 as catalysts in advance. These will produce the same counterions as the anions of the salts. AcClO_4 polymerized both monomers instantaneously after a short induction period at a concentration as low as 0.010 mmol/l (see Figure 2). When 0.10

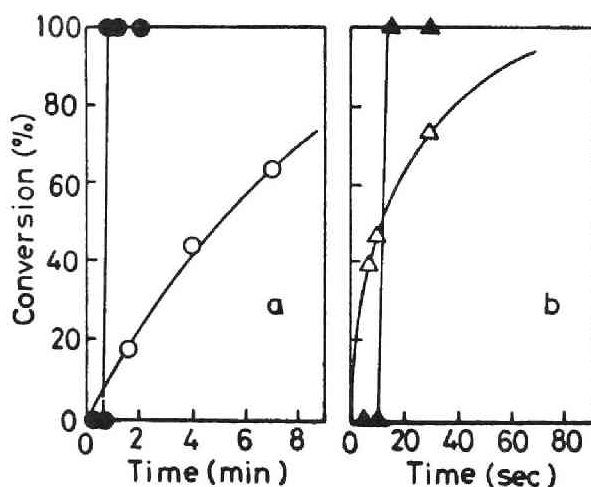


Figure 2. Time-conversion curves in the polymerization of CEVE and pMOS catalyzed by AcClO_4 and AcBF_4 in methylene chloride at 0°C ; $[\text{M}]_0$, 0.50 mol/l; (a) CEVE; (b) pMOS; \bullet , \blacktriangle , $[\text{AcClO}_4]_0$, 0.010 mmol/l; \circ , \triangle , $[\text{AcBF}_4]_0$, 0.10 mmol/l.

mmol/l AcBF_4 was used polymerization proceeded at a rate of 14%/min for CEVE and 250%/min for pMOS. Accordingly, the order of catalytic activity lies as follows: $\text{AcClO}_4 \gg \text{AcBF}_4 \gg \text{I}_2$.

The effect of $n\text{-Bu}_4\text{NClO}_4$ on the polymerization rate of the iodine system is shown in Figure 3. The presence of $n\text{-Bu}_4\text{NClO}_4$

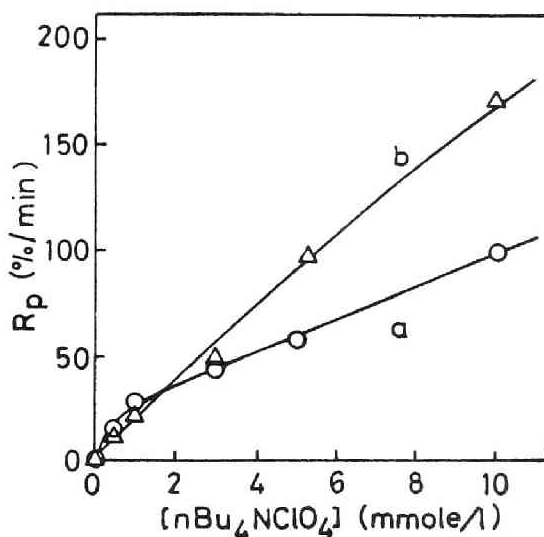


Figure 3. The effect of $n\text{-Bu}_4\text{NClO}_4$ on the polymerization rate of CEVE and pMOS catalyzed by iodine in methylene chloride at 0°C : $[\text{M}]_0$, 0.50 mol/l; a(o), CEVE, $R_{p,0} = 0.17\%/min$; b(Δ), pMOS, $R_{p,0} = 1.4\%/min$.

leads to a remarkable increase in the reaction rate; the ratio of the rates $R_p/R_{p,0}$ when 10.0 mmol/l of $n\text{-Bu}_4\text{NClO}_4$ is present and absent, is about 600 for CEVE and about 120 for pMOS. The acceleration is observed also in the presence of $n\text{-Bu}_4\text{NBF}_4$, but the extent is small compared with the acceleration by $n\text{-Bu}_4\text{NClO}_4$ (see Figure 4). The acceleration ratio, $R_p/R_{p,0}$, when 10 mmol/l

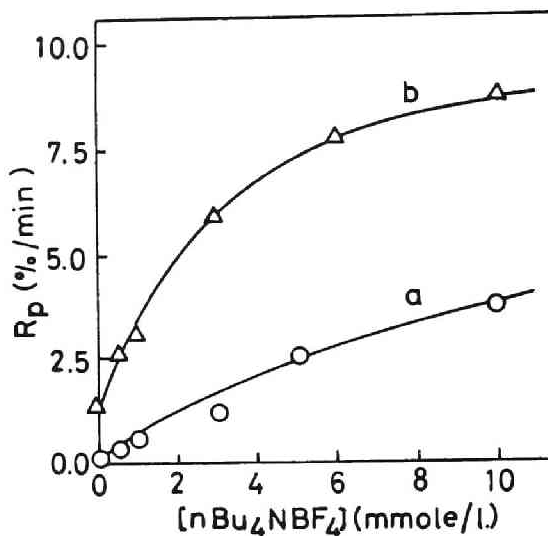


Figure 4. The effect of $n\text{-Bu}_4\text{NBF}_4$ on the polymerization rate of CEVE and pMOS catalyzed by iodine in methylene chloride at 0°C : $[\text{M}]_0$, 0.50 mol/l; $[\text{C}]_0$, 1.0 mmol/l; a(o), CEVE; b(Δ), pMOS.

of $n\text{-Bu}_4\text{NBF}_4$ is present and absent is about 23 for CEVE and about 6.3 for pMOS. Inversely, $n\text{-Bu}_4\text{NI}$ exhibits a conspicuous inhibition effect. Figure 5 shows that the polymerization of either monomer is almost completely inhibited with only 1.0 mmol/l of the salt.

The effect of $n\text{-Bu}_4\text{NClO}_4$ was examined in the polymerization of CEVE in nitrobenzene and a mixture of benzene and methylene chloride (vol ratio, 3.0:1.0) as solvents. The result is shown in Figure 6. Polymerization rate depends very little on the concentration of $n\text{-Bu}_4\text{NClO}_4$ in nitrobenzene. In the case of a mixture of benzene and methylene chloride the dependence is rather greater than in methylene chloride. In the former solvent, $R_p/R_{p,0}$ at $[\text{n-Bu}_4\text{NClO}_4] = 10 \text{ mmol/l}$ is about 1.2, and in the

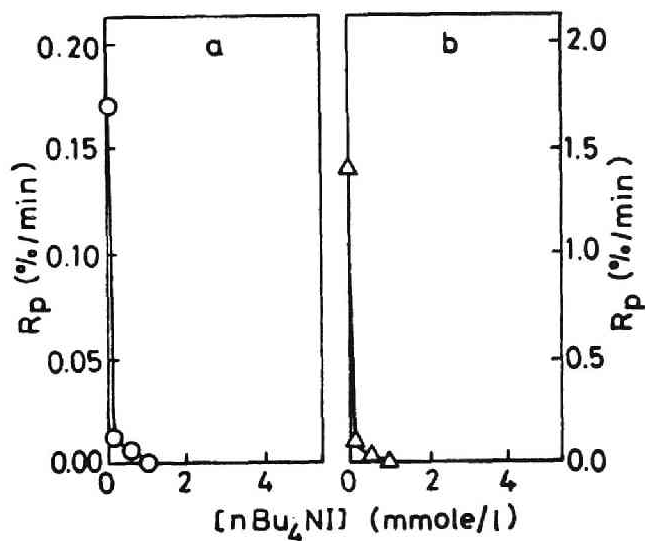


Figure 5. The effect of $n\text{-Bu}_4\text{NI}$ on the polymerization rate of CEVE and pMOS catalyzed by iodine in methylene chloride at 0°C : $[\text{M}]_0$, 0.50 mol/l; $[\text{C}]_0$, 1.0 mmol/l; a(o), CEVE; b(Δ), pMOS.

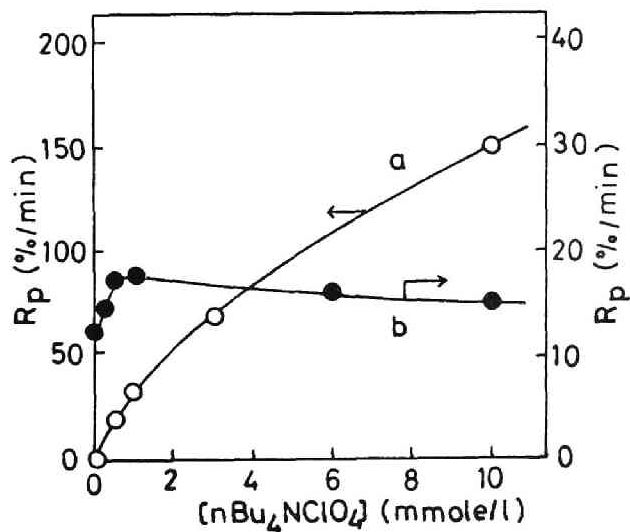


Figure 6. The effect of $n\text{-Bu}_4\text{NClO}_4$ on the polymerization rate of CEVE catalyzed by iodine at 0°C : $[\text{M}]_0$, 0.50 mol/l; $[\text{C}]_0$, 1.0 mmol/l; a(o), benzene-methylene chloride (vol ratio 3:1), $R_{p,0}=4.9 \times 10^{-3}$ %/min; b(\bullet), nitrobenzene $R_{p,0}=12\%$ /min.

latter about 3×10^4 . These values are in a sharp contrast.

The Effect of the Salts on the Molecular Weight of the polymers

90% by weight of the poly(CEVE) obtained is insoluble in a mixture of methanol and water (vol ratio, 3:1), and the viscosity number of the insoluble fraction was measured (see Table I). The viscosity of poly(CEVE) obtained with the three catalysts is in the sequence $I_2 < AcClO_4 < AcBF_4$. As seen from Figure 7,

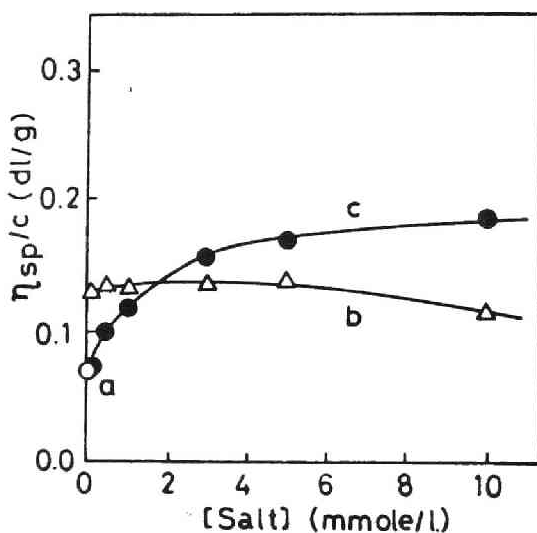


Figure 7. The effect of the salts on the molecular weight of poly(CEVE) obtained in methylene chloride at 0°C: $[M]_0$, 0.50 mol/l; and $[C]_0$, 1.0 mmol/l (measurement of η_{sp}/c : temp, 30°C benzene, 1.00 g/dl); a(○), no salt; b(Δ), $n-Bu_4NClO_4$; c(●), $n-Bu_4NBF_4$.

when $n-Bu_4NClO_4$ is present in the system with the iodine

catalyst, the viscosity number is about 0.13 and constant, independent of the salt concentration. Meanwhile, with increasing addition of $n\text{-Bu}_4\text{NBF}_4$, the viscosity number increased gradually and reached about 0.19. The sequence of viscosity increase, that is, no added salt $< n\text{-Bu}_4\text{NClO}_4 < n\text{-Bu}_4\text{NBF}_4$ corresponds well with the sequence, $\text{I}_2 < \text{AcClO}_4 < \text{AcBF}_4$.

The poly(pMOS) obtained is precipitated quantitatively in methanol. The dependence of the viscosity on the kind of catalyst is the same as that of poly(CEVE) (see Table I). The effect of the salts is shown in Figure 8. The addition of

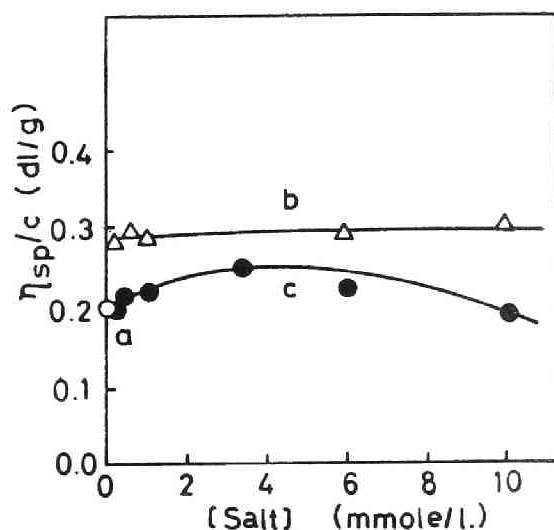


Figure 8. The effect of the salts of the molecular weight of poly(pMOS) obtained in methylene chloride at 0°C : $[\text{M}]_0$, 0.50 mol/l; $[\text{C}]_0$, 1.0 mmol/l (measurement of η_{sp}/c : temp, 30°C ; benzene, 2.00 g/dl); a(o), no salt; b(Δ), $n\text{-Bu}_4\text{NClO}_4$; c(\bullet), $n\text{-Bu}_4\text{NBF}_4$.

$n\text{-Bu}_4\text{NClO}_4$ to the iodine-catalyzed system gives rise to an in-

Table I. Viscosity numbers of resultant polymers
in methylene chloride at 0°C: $[M]_0$,
0.50 mol/l

Polymer	Catalyst	Conversion, %	η_{sp}/c , ^{a)} dl/g
Poly(CEVE)	I_2	25.5	0.068
		50.6	0.072
	$AcClO_4$	100	0.189
	$AcBF_4$	44.1	0.211
		79.3	0.237
Poly(pMOS)	I_2	18.3	0.182
		44.3	0.218
	$AcClO_4$	100	1.08
	$AcBF_4$	39.3	3.98
		73.4	4.71

a) Measurement conditions: benzene, 30°C; concn of
poly(CEVE), 1.00 g/dl; concn of poly(pMOS),
2.00 g/dl.

crease in the viscosity number (from 0.20 to 0.29) regardless of the amount of salt. In the case of $n-Bu_4NBF_4$, however, the viscosity numbers did not increase significantly, and when an excessive amount of $n-Bu_4NBF_4$ was present the viscosity number decreased. This could be explained by the action of the salt as a chain-transfer agent, as is also seen in the previous chapter.⁹

Discussion

The above-mentioned results are summarized in Table II. These results have made clear that salts such as $n\text{-Bu}_4\text{NClO}_4$, $n\text{-Bu}_4\text{NBF}_4$, and $n\text{-Bu}_4\text{NI}$ greatly influence not only the reaction

Table II. Summary of changes in polymerization rate and molecular weight with the addition of the salts^{a)}

		$n\text{-Bu}_4\text{NClO}_4$	$n\text{-Bu}_4\text{NBF}_4$	$n\text{-Bu}_4\text{NI}$
CEVE	R_p	$\uparrow\uparrow$	\uparrow	\downarrow
	MW	$\uparrow\rightarrow$	\nearrow	—
pMOS	R_p	$\uparrow\uparrow$	\uparrow	\downarrow
	MW	$\uparrow\rightarrow$	\nearrow	—

a) Catalyst, I_2 ; solvent, CH_2Cl_2 .

rate but also the molecular weight of the polymers obtained in the cationic polymerization catalyzed by iodine.

Among the three catalysts, AcClO_4 , AcBF_4 , and iodine, the order of the polymerization rate of CEVE and pMOS is $\text{AcClO}_4 \gg \text{AcBF}_4 \gg \text{I}_2$ and that of molecular weight $\text{AcBF}_4 > \text{AcClO}_4 > \text{I}_2$. The presence and absence of the salts, $n\text{-Bu}_4\text{NClO}_4$ and $n\text{-Bu}_4\text{NBF}_4$ produces the same sequences for both polymerization rate and

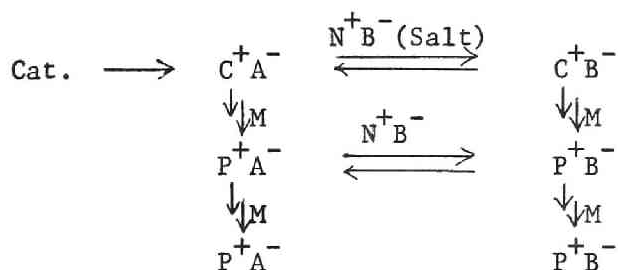
molecular weight with few exceptions. This is a strong indication that a counterion other than that formed from catalyst is present during polymerization. It can be said that iodine has proved to be a good catalyst to test the exchange of a counterion since the acceleration is clearly observed when a salt having a stable anion is used.

A trace of $n\text{-Bu}_4\text{NI}$ retarded significantly the iodine-catalyzed polymerization, which might mean that the counterion is a polyiodide ion, I_n^- and not monoiodide ion, I^- . Monoiodide ion will be too unstable to serve as a counterion in cationic polymerization in the usual solvents.

The acceleration effect in polymerization rate of pMOS is greater than that of CEVE. This means that the polymerization rate of pMOS is more sensitive to the kind of counterion involved. The fact that the acceleration effect is greater in a less polar solvent means that a counterion exists nearer to the propagating end and polymerization rate depends more on the kind of counterion in a less polar solvent. Especially in nitrobenzene, a counterion seems to exist at so distant a position as to hardly affect the polymerization rate, owing to the solvation power as well as ionization power of the solvent. This reasoning is supported by the fact that the copolymer composition in the cationic copolymerization of CEVE and styrene derivatives¹³ is influenced very much by the kind of catalyst in toluene or methylene chloride but little in nitrobenzene.

In this study, it has been made clear that the kind of catalyst brings about a great change not only in the polymerization rate but also in the molecular weight of polymer and that the added salts behave in a very similar manner. From these results, it is concluded that a counterion other than

that formed from the catalyst used also exists when a salt is added. Hence, the propagating species in the presence of a salt can be illustrated as in Scheme I.



Scheme I

If a counterion does not exchange during propagation at all, a mixture of polymers with different structures and properties will be produced owing to the presence of two kinds of separate counterions. This problem will be discussed in the next chapter.

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Chapter 12

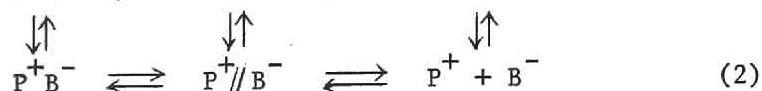
Molecular Weight Distribution of Polystyrene Formed in Two-counterion Systems

Introduction

The presence of a counterion is one of the characteristics in cationic polymerization, and that is not the case for radical polymerization. The counterion often has great influence on the propagation reaction in cationic polymerization. This is confirmed by the large effect of catalyst on the rate constant ratios involving propagation rate constant k_p , such as monomer transfer constant ratio, and on the steric structure of a polymer produced.

Though the influence of a counterion reveals itself in many respect in cationic polymerization, there have been few unequivocal knowledges about the state of a propagating end. This presents a contrast to anionic polymerization, in which the existence of various ionic species is confirmed and their propagation rate constants are measured for each ionic species. This kind of study has contributed to the elucidation of the nature of a propagating end in anionic polymerization.

When a monomer is polymerized in the presence of two kind of catalysts, it would be probable that two kinds of counterions exist at the same time. The same thing is expected with a combination of a catalyst and a neutral salt, since a salt and an acid can easily exchange their ions each other in solution. In the presence of two kinds of counterions, the following propagating species may exist according to the dissociation equilibrium of a propagating carbocation and a counterion:



If the exchange of a counterion (the reactions in the longitudinal direction in eq 1 and 2) is slow enough compared with propagation reaction, then two kinds of active species propagate independently, and in consequence a mixture of polymers having different structures or properties will be produced. On the other hand, either in the case that the exchange of a counterion is rapid enough, or in the case that the propagating end is a free ion and unaffected by a counterion, a polymer with a single and homogeneous structure or property will be obtained.

It is reported that the interchange of ion pairs is very rapid.¹ In fact, there have been no reports in cationic polymerization which indicate that the propagating chains with a different counterion grow independently in a homogeneous solution. Therefore, it seems very interesting to obtain a knowledge about the interchange rate of ion pairs in a polymerization system.

As is well known, copolymerization is a polymerization in which two kinds of monomers react with the propagating ends consisting of one kind of counterion, and it produces a variety of copolymers or a mixture of homopolymers. The concept is extended to "two-counterion polymerization". That is, two-counterion polymerization is defined as a polymerization in which a single kind of monomer reacts with two kinds of propagating ends composed of the same carbocation but of two different counterions. It would be of great interest if a mixture of polymers different in a structure is produced in two-counterion polymerization.

Pepper and Reilly² reported that the polystyrene formed by perchloric acid as catalyst has a large value of M_w/M_n such as 12. The mode of molecular weight distribution of this polystyrene might be of great interest. For, there has been no instance that such a large value of M_w/M_n was obtained by a homogeneous catalyst. It may be probable that more than one kind of propagating ends coexist at the same time in this system and they produce independently two kinds of polymers possessing different molecular weights.

In this study, making use of molecular weight distribution (MWD) as an observable polymer property, the possibility is investigated that propagation reaction proceeds independently through two kinds of active species in the cationic polymerization of styrene. The molecular weight of a polymer formed, which is determined principally by the ratio of propagation rate to monomer transfer rate, will serve as a good measure of the state of a propagating end. Further, to investigate the possibility that two kinds of active species are formed from a single catalyst, MWD of polystyrene produced by acetyl perchlorate (AcClO_4) will be discussed. For, AcClO_4 is anticipated to behave as catalyst similarly to perchloric acid.

Experimental

The syntheses and purifications of monomer, catalysts, salts and solvents were described in the previous chapters.³⁻⁵ Polymerization procedure is the same as described in the previous chapter.⁵ In all cases, polymerization was performed with the initial monomer concentration of 1.00 mol/l and at 0°C.

MWD was measured by gel permeation chromatography. The chromatograms were obtained with a Shimadzu Model GPC-1A chromatograph fitted with five columns of crosslinked polystyrene gel having pore sizes of 10^1 , 10^2 , 10^3 , 10^4 and 10^5 Å. Samples were submitted for analysis as 0.15% solution in tetrahydrofuran.

Results and Discussion

MWD of Polystyrenes Produced in Cationic Polymerization

At first, two typical examples of MWD of polystyrene obtained in cationic polymerization are shown in Figure 1. The polymerization catalysts of Figures 1-a and 1-b are boron trifluoride diethyl etherate (BF_3OEt_2) and AcClO_4 , respectively. The former is a metal halide and the latter does not comprise a metal. In the case of AcClO_4 , excess of $n\text{-Bu}_4\text{NClO}_4$ was added due to the reason which will be mentioned in the last section. In both cases the solvent is methylene chloride. The molecular weights of the polymer are very different each other, but both distribution curves are represented by a unimodal exponential distribution function. In the latter curve M_w/M_n is 1.9, which means that the curve is approximated to most probable distribution function. A similar distribution has been observed when stannic chloride (equimolar trichloroacetic acid as a cocatalyst) ($\text{SnCl}_4 \cdot \text{TCA}$) was employed as catalyst. In these systems, it is considered that there is only one propagating active species.

Two-counterion Polymerization in Methylene Chloride

MWD of the polymer obtained in methylene chloride by stannic chloride (SnCl_4) (a trace of water in the system may work as

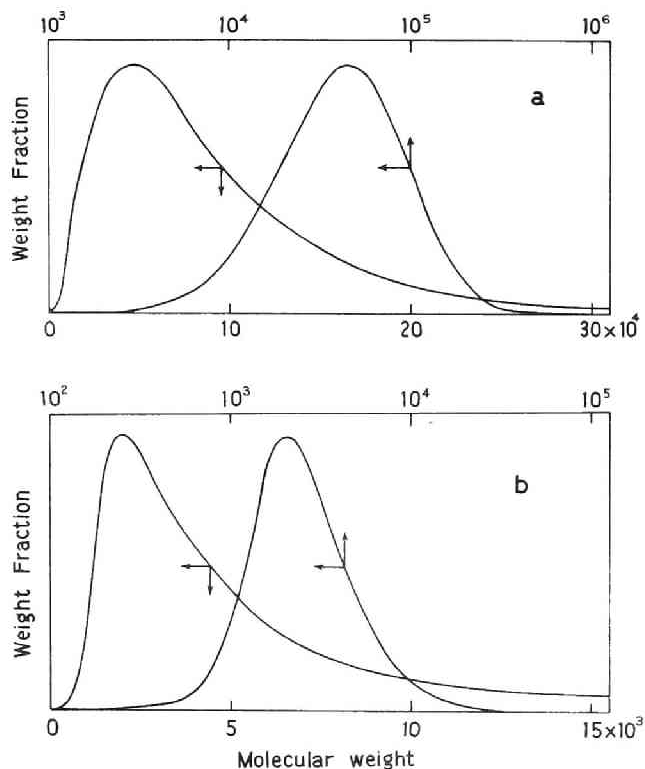


Figure 1. MWD of polystyrene catalyzed by BF_3OEt_2 or AcClO_4 in methylene chloride. a, $[\text{BF}_3\text{OEt}_2]_0$ 5.0 mmol/l; b, $[\text{AcClO}_4]_0$ 0.37 mmol/l, $[\text{Salt}]$ 1.0 mmol/l.

cocatalyst) has a single peak with a gentle slope on the low molecular weight side (Figure 2, curve a). When a trace of $n\text{-Bu}_4\text{NClO}_4$ is allowed to exist in the polymerization system, MWD becomes very broad, and is conjectured to be composed of two peaks (Figure 2, curves b-d). In the presence of still more amount of $n\text{-Bu}_4\text{NClO}_4$, MWD reduces to a single peak in a different molecular weight region from that without the salt (Figure 2, curve e). This MWD coincides well with that of the polystyrene formed by a combination of AcClO_4 and $n\text{-Bu}_4\text{NClO}_4$.

The low molecular weight peak in curves b-d seems to be concerned with perchlorate ion. Meanwhile, the high molecular

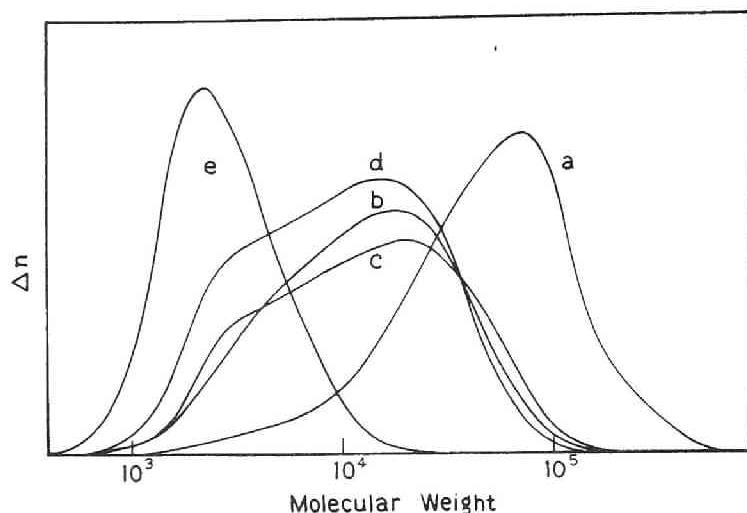


Figure 2. MWD of polystyrene obtained by SnCl_4 in the presence of $n\text{-Bu}_4\text{NClO}_4$ in methylene chloride. $[\text{C}]_0$ 5.0 mmol/l; $[\text{Salt}]$, mmol/l: a 0.0, b 0.25, c 0.50, d 1.0, e 5.0.

weight peak does not coincide with curve a, the MWD of a polymer produced by SnCl_4 . This might be explained as follows: coexistence of SnCl_4 and perchlorate ion will lead to the formation of a complex which is capable to behave as a counterion. If a propagating species comprising the complex-type counterion is enough reactive compared with that of the counterion formed from SnCl_4 and water, a peak corresponding to curve a will vanish. In fact, the addition of a small amount of $n\text{-Bu}_4\text{NClO}_4$ to the SnCl_4 catalyst system brings about a large acceleration of the reaction rate, as was described previously.⁵

In order to ascertain the above-mentioned inference, the polymerization by a catalyst mixture of SnCl_4 and AcClO_4 was carried out. The polymerization rate at $[\text{SnCl}_4] = 10$ mmol/l is about the same as that at $[\text{AcClO}_4] = 0.50$ mmol/l. When a mixture

of SnCl_4 (5.0 mmol/l) and AcClO_4 (0.25 mmol/l) is made use of, the polymerization proceeds about 50 times as quickly as those by each single catalyst. And the MWD of the formed polystyrene are very broad, the peaks of which are situated in an intermediate position between the peaks for each single catalyst (Figure 3, curves b-d). The position of these peaks is about the same as those of polymers obtained by SnCl_4 and $\text{n-Bu}_4\text{NClO}_4$ (Figure 2, curves b-d). This confirms the formation of a reactive propagating end from SnCl_4 and perchlorate. The wide distribution of curves b-d in Figure 3 may be caused by the presence of three different active species, i.e., a complex-type counterion formed from AcClO_4 and SnCl_4 and two kinds of counterions from AcClO_4 .

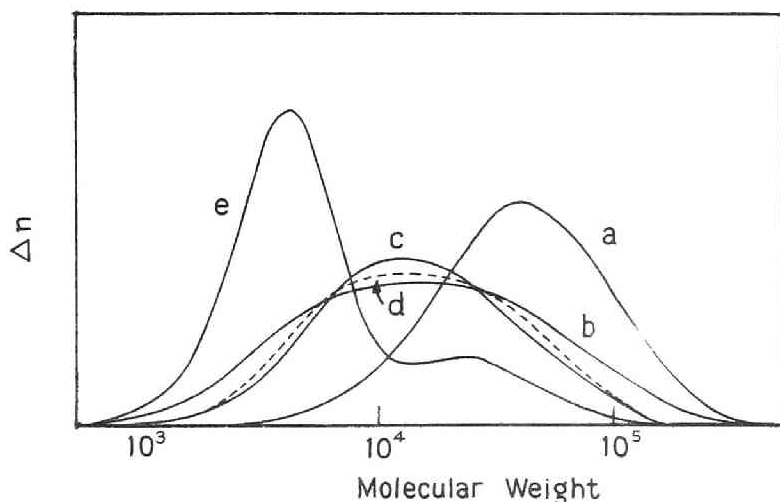


Figure 3. MWD of polystyrene obtained by a mixture of SnCl_4 and AcClO_4 in methylene chloride. $[\text{SnCl}_4]$, mmol/l: a 10.0, b 7.5, c 5.0, d 2.5, e 0.0; $[\text{AcClO}_4]$, mmol/l: a 0.0, b 0.12, c 0.25, d 0.37, e 0.50.

Next, polymers obtained by BF_3OEt_2 in the presence of $n\text{-Bu}_4\text{NClO}_4$ were examined. Both MWD with $n\text{-Bu}_4\text{NClO}_4$ equivalent to the catalyst and without $n\text{-Bu}_4\text{NClO}_4$ show unimodal shapes though their average molecular weights are very different (Figure 4, curves a and c). In the presence of $n\text{-Bu}_4\text{NClO}_4$ 1/10 equivalent to the catalyst, the polymer has a broad distribution, probably consisting of two peaks. One of those is thought to fit to curve c and the other to an imaginary peak at a middle position between curves a and c.

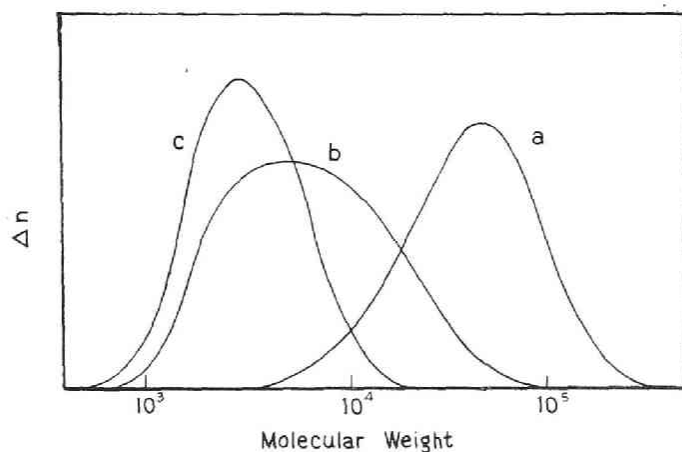


Figure 4. MWD of polystyrene obtained by BF_3OEt_2 in the presence of $n\text{-Bu}_4\text{NClO}_4$ in methylene chloride. $[\text{C}]_0$ 5.0 mmol/l; $[\text{Salt}]$, mmol/l: a 0.0, b 0.50, c 5.0.

From these results, it is concluded that two active species whose counterions are $\text{MX}_n\text{-ClO}_4^-$ and ClO_4^- , propagate separately when an adequate amount of $n\text{-Bu}_4\text{NClO}_4$ or AcClO_4 is used together

with metal halide (MX_n).

Two-counterion Polymerizations in Nitrobenzene and in a Mixture of Methylene Chloride and Benzene

A phenomenon was found, as described in the above section, that two propagating species yield a polymer of different molecular weights separately. It was investigated whether this holds also in nitrobenzene as a solvent, since it has a greater polarity. In Figure 5 are shown MWD of polystyrene obtained by SnCl_4 in the coexistence of $n\text{-Bu}_4\text{NClO}_4$. In this case, despite the change in the quantity of $n\text{-Bu}_4\text{NClO}_4$, the broadness of MWD hardly varies. Merely average molecular weight decreases with the increase in the concentration of $n\text{-Bu}_4\text{NClO}_4$. The possibility that two peaks are overlapping is denied clearly.

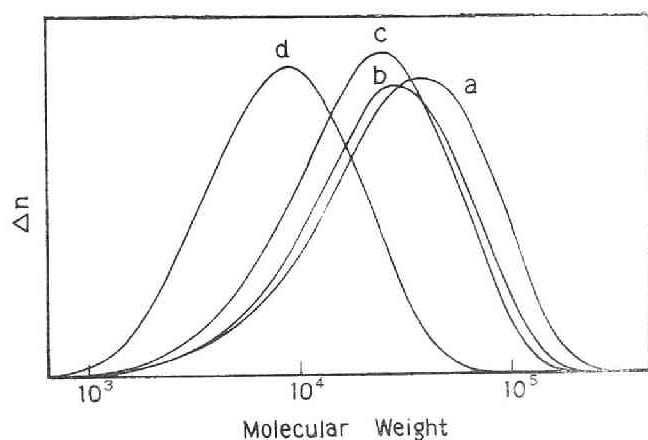


Figure 5. MWD of polystyrene obtained by SnCl_4 in the presence of $n\text{-Bu}_4\text{NClO}_4$ in nitrobenzene. $[\text{C}]_0$ 5.0 mmol/l; $[\text{Salt}]$, mmol/l: a 0.0, b 0.25, c 0.50, d 5.0.

In the polymerization catalyzed by SnCl_4 in nitrobenzene, the addition of $n\text{-Bu}_4\text{NClO}_4$ leads to the change in average molecular weight of the polymer, and furthermore the presence of $n\text{-Bu}_4\text{NClO}_4$ more than the amount of catalyst results into an identical MWD with that yielded by AcClO_4 . This indicates that a counterion has bearing on propagation reaction also in nitrobenzene. It can, however, be said that the influence of counterion is rather small, as the molecular weight does not change so largely with the addition of the salt as in methylene chloride. Moreover, the broadness of MWD is fixed and unrelated to the quantity of the salt. Hence, it is concluded that a counterion is connected relatively loosely and exchanges rapidly enough during propagation reaction in nitrobenzene as a solvent.

Benzene could be applied as a nonpolar solvent. However, most of the polymer formed in benzene in the presence of $n\text{-Bu}_4\text{NClO}_4$ is methanol-soluble oligomer. Therefore, a mixture of methylene chloride and benzene (3:1 vol ratio) was used as a nonpolar solvent. The dependence of MWD on the concentration of $n\text{-Bu}_4\text{NClO}_4$ is shown in Figure 6. Without the salt, MWD is bimodal, which suggests that an aggregate ion exists as one of counterions. When the added salt is equivalent to the amount of the catalyst, MWD (curve d) coincides with that obtained by AcClO_4 as catalyst. If $n\text{-Bu}_4\text{NClO}_4$ 1/10 as much as the catalyst is present, the reaction is accelerated and MWD (curve c) shows a single peak. This indicates that a complex formed by SnCl_4 and perchlorate ion is a principal counterion in the system.

Some Considerations on Two-counterion Polymerization

The results in this study are summarized as follows: 1) in the cationic polymerization of styrene, two active species pro-

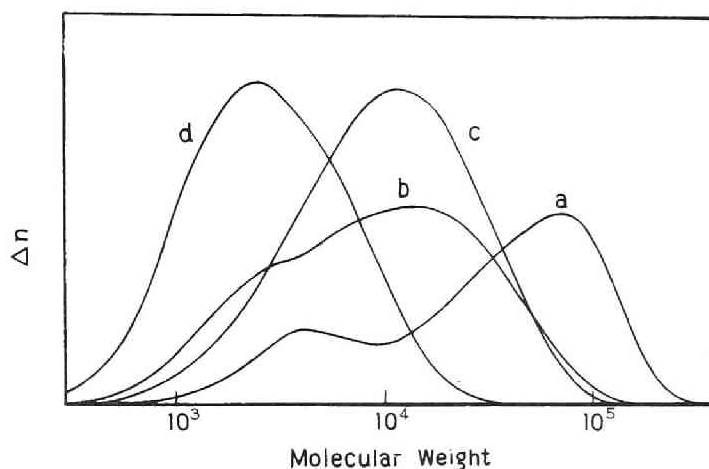


Figure 6. MWD of polystyrene obtained by SnCl_4 in the presence of $\text{n-Bu}_4\text{NClO}_4$ in a mixture of methylene chloride and benzene (3:1 vol ratio). $[\text{C}]$ 5.0 mmol/l; $[\text{Salt}]$, mmol/l: a 0.0, b 0.25, c 0.50, d 5.0.

pagate separately in methylene chloride, but only one species, apparently, exists in nitrobenzene owing to rapid exchange of counterion, 2) metal halides such as SnCl_4 and BF_3OEt_2 form with perchlorate ion a complex which works as a counterion. It would be of great importance that knowledges were obtained as the tightness of the bond between a carbocation and counterion in this way.

In this experiment, the formation of a complex impedes more or less the anticipated two-counterion polymerization. If two kinds of Lewis acids and a cocatalyst are utilized, it will be probable that two counterions are produced independently from each Lewis acid through the interaction with a cocatalyst, and so two-counterion polymerization will be achieved successfully. Unless a cocatalyst is made use of, the two catalysts might interact and be followed by the complexity of the system,

as reported by Marek and Chmelir.⁶ The two kinds of catalysts should be selected so as to produce polymers very different in a molecular property such as molecular weight, steric structure and geometric structure.

MWD of Polystyrene Obtained by AcClO_4

As seen from Figure 7, the molecular weight distributions of polystyrene obtained by AcClO_4 consisted of two distinct peaks. The proportion of the lower molecular weight fraction increases as conversion increases. Therefore, such molecular weight distributions are not due to the formation of a branched polymer.

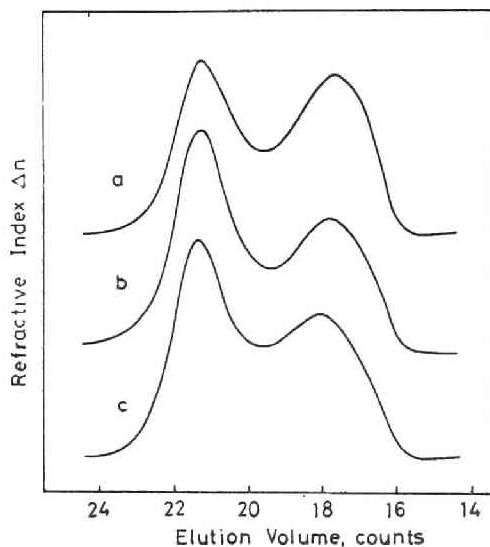


Figure 7. Gel permeation chromatograms of polystyrene formed by AcClO_4 (Marks correspond to those of Table I).

When 0.050 mmol/l $n\text{-Bu}_4\text{NClO}_4$ was added to the polymeriza-

tion system, the proportion of the higher molecular weight fraction was considerably reduced (Figure 8, curve d). Relative magnitudes of both peaks vary but their position and shape do not change. Addition of 0.10 mmol/l of the salt reduced the higher molecular weight fraction still further and the peak vanished entirely when 1.0 mmol/l salt was added (Figure 8, curves e and f).

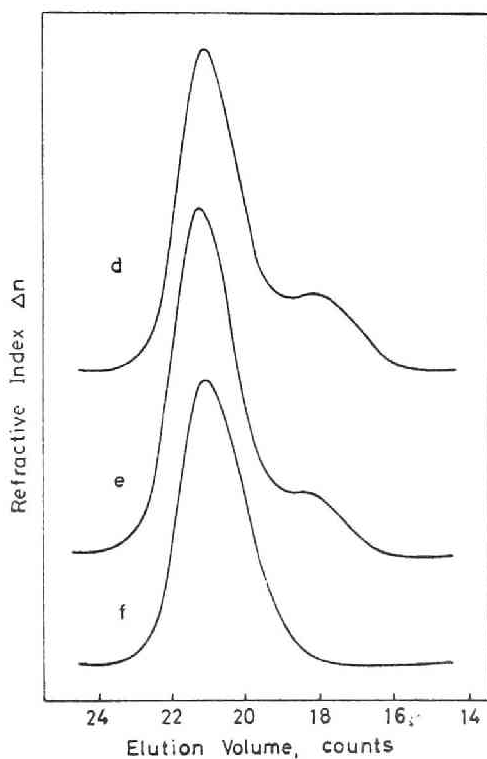


Figure 8. Gel permeation chromatograms of polystyrene formed by AcClO_4 in the presence of $n\text{-Bu}_4\text{NClO}_4$ (Marks correspond to those of Table I).

The values of number-average molecular weight (M_n), weight-average molecular weight (M_w), and the ratio (M_w/M_n) are calculated from Figures 7 and 8, and these values are summarized in Table I. M_w/M_n is below 2.0 for systems consisting of one peak, while the value is above 3.0 for the systems having a two-peak distribution. On the other hand, Pepper and Reilly² performed the cationic polymerization of styrene at -30°C using perchloric acid which involves the same anion as AcClO_4 . M_n and M_w of the polystyrene obtained were measured by cryoscopy and light scattering, respectively. The ratio M_w/M_n was about 12, which is much larger than that of our samples.

The addition of $n\text{-Bu}_4\text{NClO}_4$ does not affect the position and shape of either peak in the AcClO_4 system. It only brings about a change in relative magnitudes of both peaks. Consequently, it is possible to separate the peaks using the single peak of the polymer prepared at high salt concentration. M_n , M_w , and M_w/M_n of the separated peaks were calculated. In addition the number fractions of molecules of the lower and higher molecular weight parts were obtained. As shown in Table II, the values of M_n and M_w are almost constant, independent of conversion and the amount of salt added, for both higher and lower molecular weight fractions. The molecular weights of the two fractions are very different, which leads one to consider the presence of two propagating species. In the absence of the salt, the number fraction of lower molecular weight part is ca. 0.9, and predominant.

It is not clear yet from the above-mentioned results why AcClO_4 , peculiarly, gives the polystyrene with bimodal molecular weight distribution. It could not be, however, denied that two kinds of propagating species (counterions) coexist in the poly-

Table I. Average molecular weights, M_n and M_w , and the ratio M_w/M_n of the polystyrenes obtained by AcClO_4 (Polymerization conditions: $[\text{M}]_0$, 1.0 mol/l; $[\text{C}]_0$, 0.37 mmol/l; solvent, CH_2Cl_2 ; 0°C)

	$[\text{n-Bu}_4\text{NClO}_4]$, mmol/l	Time, min	Conv, %	M_n	M_w	M_w/M_n
a	—	30	37.0	3780	13600	3.60
b	—	50	50.7	3060	11200	3.66
c	—	81	71.4	3250	10800	3.32
d	0.05	45	39.1	2490	6190	2.49
e	0.10	45	41.0	2280	4920	2.16
f	1.0	60	41.9	2070	3090	1.49

Table II. M_n , M_w , and M_w/M_n of the separated fractions of the polystyrenes

	Lower molecular weight peak				Higher molecular weight peak			
	M_n	M_w	M_w/M_n	Number fraction	M_n	M_w	M_w/M_n	Number fraction
a ^{a)}	2076	3099	1.49	0.875	15800	23400	1.49	0.125
b	2030	3063	1.51	0.933	17400	24100	1.39	0.067
c	2075	3088	1.49	0.906	14500	21300	1.47	0.094
d	2123	3118	1.47	0.974	16200	21300	1.31	0.026
e	2082	3092	1.49	0.985	16400	20100	1.23	0.015
f	2070	3090	1.49	1.000	—	—	—	0.000

a) Marks correspond to those of Table I.

merization and each type of chain propagates independently until propagation is interrupted. We might consider as the pairs of counterions, simple ion and aggregate ion, anhydrous ion and hydrated ion, and so on. This interesting problem remains unsolved, future investigation being desired.

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6

SUMMARY

The studies collected in this thesis are concerned with cationic polymerization of vinyl ethers and styrene derivatives. Propagation reaction of the polymerization has been investigated on the basis of structure and reactivity of monomers and propagating species. The experimental results shown in Parts I-IV will be summarized below.

PART I Cationic Copolymerization of 2-Chloroethyl Vinyl Ether with Styrene Derivatives

Chapter 1 Characteristics in the Copolymerization of a Vinyl Ether with Styrene Derivatives

The possibility of copolymer formation and the effect of polymerization conditions on monomer reactivity ratios (MRR) were investigated for cationic copolymerizations of a vinyl ether with styrene derivatives. 2-Chloroethyl vinyl ether (CEVE) was used as the vinyl ether, and p-methoxystyrene (pMS), p-methylstyrene (pMS) and α -methylstyrene (α MS) as the styrene derivatives. Copolymerization was carried out in toluene or methylene chloride, being catalyzed by boron trifluoride diethyl etherate (BF_3OEt_2) or stannic chloride with equimolar trichloroacetic acid ($\text{SnCl}_4 \cdot \text{TCA}$) at -78°C . The copolymer composition was determined from each monomer consumption through gas chromatography. The copolymer formation was confirmed by fractionation and nmr spectrum of the product. In CEVE- α MS system, the relative reactivity of each monomer was independent of the kind of the propagating chain ends ($r_1 \times r_2 \simeq 1$). In

contrast, composition curves showed an S-shape in CEVE-pMOS and CEVE-pMS system ($r_1 \times r_2 > 1$). It was found that polymerization conditions significantly affect MRR; the CEVE content in the copolymer was greater by BF_3OEt_2 than by $\text{SnCl}_4 \cdot \text{TCA}$.

Chapter 2 Temperature Dependence of Monomer Reactivity Ratios

Temperature dependence of monomer reactivity ratios, r_1 and r_2 , and their product $r_1 \times r_2$ were studied in the cationic copolymerization of CEVE (M_1) with styrene derivatives (M_2) (pMOS, pMS and α MS). Methylene chloride, toluene and benzene were used as solvent, and $\text{SnCl}_4 \cdot \text{TCA}$ and BF_3OEt_2 were used as catalyst. r_1 increased and r_2 decreased with increasing polymerization temperature in the copolymerizations except that of CEVE with pMOS. On the other hand, r_1 and r_2 hardly depended on polymerization temperature in the mutual copolymerization between vinyl ethers or styrene derivatives. On the basis of these results, the difference in the transition state of the propagation reaction of vinyl ethers and styrene derivatives was discussed.

Chapter 3 Effects of Solvent and Catalyst on Relative Reactivity

The change in relative reactivity in the cationic copolymerization of CEVE with styrene derivatives (pMOS, pMS and α MS) was investigated with various catalysts and solvents. The styrene content in the copolymers increased when a polar solvent and/or a strong catalyst were used. The change of relative reactivity in the copolymerization of CEVE with the styrene derivatives was much greater than that in the mutual copolymerization between

the homologues of vinyl ethers or styrene derivatives. When nitroethane was used as a solvent, not only the polarity but also the nucleophilicity influenced the copolymer composition. The results were discussed by two energies, E^π and E_{rs} , which are measures of complex formation between monomer and carbocation, and stabilization energy in the transition state, respectively.

PART II Substituent Effect in Cationic Polymerization of Vinyl Ethers and Styrenes

Chapter 4 Effect of β -Substituents on Reactivity

In order to know the effect of β -methyl substitution, cationic copolymerizations of isobutyl vinyl ether (IBVE) with isobutyl propenyl ether (IBPE) and of pMOS with anethole were performed. The changes in relative reactivity with two different solvents, catalysts, or temperatures were examined. The order of reactivity was generally as follows: $\text{cis-IBPE} > \text{IBVE} > \text{trans-IBPE}$, and $\text{pMOS} > \text{trans-anethole} > \text{cis-anethole}$. In a more polar solvent, by a stronger catalyst and/or at a higher temperature, the reactivities of both of the three monomers became close to each other. The results were interpreted in terms of "reduction of selectivity" and "localization of charge".

Chapter 5 Effect of α -Substituents on Reactivity

To gain a knowledge of the cationic polymerizability of α,α -disubstituted ethylenes, homopolymerization of α -substituted vinyl ether and styrene, and also copolymerization with the corresponding α -unsubstituted monomers were carried out.

Methyl, ethyl, ethoxy and phenyl groups were introduced as α -substituent. Ethyl α -methylvinyl ether and α -methylstyrene produced homopolymers but ethyl α -ethylvinyl ether, α -ethylstyrene, α -ethoxystyrene did not. In the copolymerization, all of these α,α -disubstituted monomers were found to have greater reactivities for unsubstituted propagating end than the corresponding unsubstituted monomers do. It was concluded that α,α -disubstituted ethylene suffers steric hindrance in cationic polymerization more than the corresponding α,β -disubstituted one does, contrary to radical polymerization. The change in reactivity of vinyl compounds with α -methyl substitution in electrophilic reactions was discussed.

Chapter 6 Reactivity of 2-Alkoxybutadienes

Molecular structure, molecular properties and cationic polymerizability of 2-alkoxybutadienes, which are α -vinyl-substituted vinyl ethers, were investigated. Methoxy-, ethoxy-, isopropoxy-, tert-butoxy- and 2-chloroethoxybutadienes were synthesized. Uv, ir and nmr spectra of the 2-alkoxybutadienes except 2-(tert-butoxy)butadiene showed that the diene and the alkoxy group are coplanar. It was, however, suggested that 2-(tert-butoxy)butadiene cannot take a planar conformation owing to steric hindrance. Cationic homopolymerization of 2-ethoxybutadiene resulted principally into the formation of a methanol-soluble oligomer. The relative reactivities of the 2-alkoxybutadienes against the ethyl vinyl ether propagating end were determined by the copolymerization with ethyl vinyl ether, and the following order was obtained: isopropoxy > ethoxy > 2-chloroethoxy > methoxy > t-butoxybutadiene.

Chapter 7 Comparison of Polar Bromination with Cationic Polymerization

The relative reactivity of various alkyl vinyl ethers and styrenes in polar bromination reaction was studied to compare with their relative reactivity in cationic polymerization. α -Methyl-substituted vinyl ether and styrene were 3-12 times as reactive as unsubstituted compounds. On the other hand, some β -methyl-substituted derivatives were more reactive and others are less reactive than unsubstituted ones. Though the bromine concentration at reaction was considerably low ($\sim 10^{-3}$ - 10^{-2} mol/l), the change in reactivity with introduction of a substituent was not so large as to suggest that the intermediate species is a carbocation whose charge is localized on α -carbon. The substituent effect of the bromination reaction was very similar to cationic polymerization among many electrophilic addition reactions.

PART III Structure and Reactivity of Monomers in Cationic Polymerization

Chapter 8 Theoretical Consideration on the Reactivity of Vinyl Ethers and β -Substituted Vinyl Ethers

To elucidate the propagation mechanism in the cationic polymerization of vinyl ethers and β -substituted vinyl ethers, the electron distribution in these monomers was computed by the extended Hückel method. Propylene and styrene derivatives were also studied for comparison with the vinyl ether derivatives. Attempts were made to explain the experimental results by

various calculated reactivity indices. With the unsaturated hydrocarbons, the reactivity indices on the β -carbon parallel with the relative reactivity in the cationic polymerization or oligomerization. This agreement suggests that the transition state for the rate-determining step of the propagation reaction is represented by a model in which the carbocation interacts mainly with the β -carbon of a monomer. On the other hand, the effect of β -alkyl or alkoxyl groups on the reactivity of vinyl ethers could not be explained by the model in which the carbocation interacts with an olefinic carbon or an ether oxygen, or with the two atoms. A model was proposed on the basis of the electronic stabilization energy due to the delocalization from the occupied orbital of a monomer to the vacant orbital of a carbocation. The model can explain reasonably the relative reactivity of vinyl ethers and β -substituted vinyl ethers observed in the cationic copolymerization catalyzed by BF_3OEt_2 .

Chapter 9 Molecular Properties and Reactivity of Vinyl Ethers and Styrene Derivatives

The measurement of ^{13}C nmr spectrum and the calculation of electron density of vinyl ethers and styrene derivatives have been carried out so as to study the relationships between molecular properties of monomer and reactivity in cationic polymerization. Methyl substitution on vinyl β -carbon induced an upfield shift in ^{13}C nmr spectrum and an increase in electron density of α -carbon, and vice versa for β -carbon. α -Methyl substitution functioned just in the opposite way. Chemical shifts of α - and β -carbons in alkyl vinyl ethers could not be

simply correlated with their electron densities. The reactivities of para-substituted styrenes were explained consistently by each of electron density, chemical shift and ionization potential. Propagation reaction was divided into two stages, π -complex formation and bond formation, and it was concluded that both stages are concerned with propagation. The transition state of propagation reaction is inferred to be an unsymmetrical α,β -type complex.

PART IV Salt Effect on Polymerization rate and on Molecular Weight Distribution of the Polymer

Chapter 10 Salt Effect in the Polymerization by Various Catalysts

The effects of salts were examined in cationic polymerization of vinyl compounds. Cationic polymerization of styrene was carried out at 0°C , with acetyl perchlorate, stannic chloride, $\text{SnCl}_4 \cdot \text{TCA}$ and BF_3OEt_2 as catalyst. Tetra-n-butylammonium perchlorate ($\text{n-Bu}_4\text{NClO}_4$), fluoroborate ($\text{n-Bu}_4\text{NBF}_4$) and iodide ($\text{n-Bu}_4\text{NI}$) were used as salt. The presence of small amount of the salts changed both the polymerization rate and the molecular weight of polymer appreciably. The consideration of various effects led to the conclusion that the results are explicable principally on the basis of counterion exchange. To confirm this, the copolymerization of CEVE with αMS was investigated at -78°C . When the perchlorate salt was added, the copolymer composition curve catalyzed by stannic chloride shifted and coincided with that catalyzed by acetyl perchlorate. This result supports the concept of counterion exchange.

Chapter 11 Salt Effect in the Polymerization by Iodine

The cationic polymerization of CEVE and pMOS was studied in the presence of tetra-n-butylammonium salts such as $n\text{-Bu}_4\text{NClO}_4$, $n\text{-Bu}_4\text{NBF}_4$, and $n\text{-Bu}_4\text{NI}$. The polymerization was carried out using iodine as catalyst at 0°C in methylene chloride, benzene-methylene chloride mixture, and nitrobenzene. The presence of $n\text{-Bu}_4\text{NClO}_4$ or $n\text{-Bu}_4\text{NBF}_4$ brought about an acceleration in reaction rate and an increase in the molecular weight of the polymer. As a notable example, the polymerization rate in the presence of $n\text{-Bu}_4\text{NClO}_4$ was 3×10^4 times faster than in the absence of the salt. The results of the experiment were explained by the presence of more than one counterion in the polymerization systems.

Chapter 12 Molecular Weight Distribution of Polystyrene Formed in Two-counterion Systems

To know the tightness of the bond between a propagating carbocation and counterion, polymerization of styrene was carried out in the presence of two kinds of catalysts or under the coexistence of a catalyst and a salt. The molecular weight distribution of the polystyrene was examined by gel permeation chromatography. It was found that molecular weight distribution of the polystyrene obtained in some solvents consisted of two peaks. Furthermore, acetyl perchlorate was proved to give, for itself, a polystyrene with bimodal molecular weight distribution. On the basis of these results, it was concluded that the bond of a carbocation and counterion is so tight under some conditions that exchange of counterion may not occur during propagation.

LIST OF PUBLICATIONS

Chapter 1	Polymer J., <u>1</u> , 19 (1970).
Chapter 2	Polymer J., <u>2</u> , 29 (1971).
Chapter 3	J. Macromol. Sci.-Chem., A <u>5</u> , 549 (1971).
Chapter 4	J. Polym. Sci., Part A-1, <u>10</u> , 85 (1972); J. Polym. Sci., Part A-1, submitted.
Chapter 5	Macromol. Chem., in press, (a part).
Chapter 6	To be published.
Chapter 7	Macromol. Chem., in press, (a part).
Chapter 8	J. Polym. Sci., Part A-1, <u>7</u> , 3129 (1969).
Chapter 9	J. Polym. Sci., Part A-1, submitted.
Chapter 10	J. Polym. Sci., Part A-1, <u>9</u> , 1563 (1971).
Chapter 11	Polymer J., <u>3</u> , 724 (1972).
Chapter 12	J. Polym. Sci., Part B, <u>9</u> , 783 (1971).

Other publications not transcribed to the present thesis:

Cationic Copolymerization of 3,3-Bis(chloromethyl)oxetane
with Vinyl Compounds

J. Polym. Sci., Part A-1, 7, 1115 (1969).

A Simple Index of Copolymerizability

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